

VIBRATIONAL ASSIGNMENTS FOR SOLID MALONIC ACID: KINETICS
OF THERMAL DECARBOXYLATION AND REACTIONS
OF MALONIC ACID IN ALKALI HALIDES

Dissertation

Submitted in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy
in the
Faculty of the Graduate School
of
West Virginia University

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by

Lowell Allen Cosby, B. S.

Morgantown
West Virginia
1969

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PREFACE

This dissertation consists of four separate sections: general introduction and experimental section, and three separate parts each of which contains a bibliography. Part I deals with an assignment of the infrared absorption bands of malonic acid to the fundamental vibrational motions of the molecule by use of a simplified symmetry approach. Part II deals with a study of the double decomposition reactions between malonic acid and various alkali halide salts used as the reaction media. Part III presents kinetic data obtained for the thermal decarboxylation of malonic acid in KBr and RbBr and discusses the significance of the activation parameters obtained from the data.

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INTRODUCTION AND GENERAL EXPERIMENTAL

Introduction

The original aim of this research was a kinetic study of the thermal decarboxylation of malonic acid in alkali halide media. This was to be effected by mixing malonic acid with the desired alkali halide, pressing the resultant mixture into a pellet, heating the pellet for given intervals of time and observing the amount of decomposition of the malonic acid by means of changes in its infrared spectrum. This proposed technique worked quite well in two of the alkali halide matrices studied, KBr and RbBr. In other alkali halide media the collection of useful kinetic data was impractical due to interfering side reactions between malonic acid and the chosen alkali halide. One of these side reactions, a double decomposition reaction between malonic acid and the alkali halide matrix, occurred to some extent in all of the salts used although in KBr and RbBr the extent of occurrence was small enough to be insignificant. The other side reaction, tentatively labelled solid solution formation, was found to occur only in CsCl and anhydrous NaBr.

Experimental

The following experimental procedures were, in general, used throughout this research. Certain specific experimental procedures will be cited in the separate parts of this dissertation.

Sources of Materials

Malonic acid, obtained from K and K Laboratories, Inc., Plainview, New York, was recrystallized from acetone at low temperatures (dryice-acetone or ice-water) and the resultant crystals filtered from solution, dried, and ground to a fine powder in an agate mortar. This crystalline product was shown by titration with NaOH to be 99.9% malonic acid. Prior to incorporation in alkali halide pellets, the finely ground malonic acid was placed under reduced pressure for several hours at room temperature.

Deuterated malonic acid was used as received from Strohler Isotopic Chemicals, P. O. Box 1134, Montreal 3, Canada. Although advertised as 99% pure malonic acid- d_4 , the product contained malonic acid- h_4 as evidenced by its infrared absorption spectrum which showed bands due to malonic acid- h_4 . The deuterated product also contained D_2O according to its infrared spectrum.

Alkali halides from three different sources were used. A portion of all of the salts used was obtained from Brinkman Instruments, Inc. Cantiague Road, Westbury, L. I., N. Y. These salts were manufactured by E. G. Merck, Ag., Darmstadt (Germany) under the trade labels "Suprapur" or "Ultrapur". Some of the KBr and CsI salts were obtained from Harshaw Chemicals Co., Cleveland, Ohio, 44106. At times Fisher Reagent Grade salts were also used. The experiments performed using various brands of salts exhibited no dependence upon the particular brand used.

The KOH used in the preparation of malonic acid salts was obtained from Fisher Scientific Company, Fairlawn, N. J., and was used as received.

Instruments

Most of the spectra used in this research were obtained by means of a Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl optics or by means of a Beckman Model IR-12 grating infrared spectrophotometer. The calibration of the two instruments was checked periodically by scanning the polystyrene spectrum or by scanning the single beam background spectrum. The absorption frequencies recorded from the prism instrument are accurate to $\pm 1\text{K}^*$ in the 2000-640 K region, and to $\pm 5\text{K}$ in the 4000-2000 K region. The absorption frequencies of the grating instrument have an uncertainty of $\pm 0.25\text{ K}$ from 2000-200 K and an uncertainty of $\pm 0.5\text{ K}$ from 4000-2000 K.

Pellet Preparation

Two different pellet dies were used. One was a Perkin-Elmer 13 mm circular die; the other was a Beckman 12 x 2 mm rectangular die. Both were evacuated in the pellet pressing procedure and gauge pressures of 20,000 to 30,000 pounds per square inch were used in forming the pellets. No differences in the behaviors of the products from the two pellet dies were noted; hence, in the material

*Throughout this dissertation, all frequencies will be given in Kayser (K) units ($1\text{K} = 1\text{ cm}^{-1}$).

which follows, no distinction will be made between the two types of pellets used.

A standard procedure was used in the pressing of the pellets. In the case of pellets pressed from pre-dried salts, the die was filled in a dry box and transferred to the hydraulic press. The salts which were used as received were placed in the die in a constant humidity (approximately 40% rel.) room. The die was then placed under enough pressure to seal the rubber-metal contacts and evacuated. After a few minutes of evacuation, the die was then placed under its recommended operating pressure and allowed to remain under pressure for a few minutes. The pressure on the die was then reduced and the die evacuated for a few more minutes. The die was again placed under its operating pressure. Finally, dry air was used in bringing the pressure inside the die back to atmospheric pressure. The pressure on the die was then released and the die removed from the press.

The salts used in the pressing of the pellets were either used as received or dried in the following manner. The commercial salt was ground to a very fine powder in an agate mortar. This fine powder was then placed in a flask under reduced pressure (approximately .01 torr) and held approximately 250° for several days. The flask was then filled with dry air and sealed off with a stopcock.

Two different methods of mixing the components for a pellet were used. For purposes of later reference these two procedures will be assigned numbers and described separately.

Procedure I: -- This was the routine procedure used in the preparation of the pellet mixtures for use in the kinetic study of the thermal decarboxylation reaction. Weighed amounts of pre-ground and dried alkali halide and malonic acid were placed in a 500 ml flask in a dry box. A large magnetic stirrer bar was then placed in the flask, the flask stoppered, removed from the dry box, placed on a rotary evaporator and sealed off from the atmosphere. The rotary evaporator was then started and a magnetic stirrer motor placed beneath the rotating flask. During the mixing which followed, the axes of rotation of the magnetic stirrer bar and of the rotating flask were approximately perpendicular to each other. This created a double stirring motion for mixing of the two components. After about 2 hours of vigorous mixing, the flask was removed from the rotary evaporator and stoppered. Pellets were pressed as needed from the resulting mixture.

Procedure I provided a means of dispersing the malonic acid in the alkali halide salt without the possibly harmful side effects of mixing by grinding.

Procedure II: -- This method of mixing the components consisted of placing weighed amounts of pre-ground materials in an agate mortar and mixing by light grinding action using an agate pestle.

PART I

Assignment of the Infrared Absorption Bands in Crystalline
Malonic Acid.I-1: Introduction

Upon heating a malonic acid-alkali halide pressed pellet at approximately 100° , changes take place in its infrared spectrum. These changes involve the disappearance of some absorption bands and the appearance of other bands. Comparable changes in the infrared spectrum have been ascribed¹ to the change of malonic acid from the β to the α phase, shown by differential thermal analysis,² to occur at approximately 130° . The temperature of the phase change as determined by differential thermal analysis is probably about 25° too high since the temperature of fusion, determined by standard melting point technique to be $134-136^{\circ}$ C, is shown by differential thermal analysis to be 160° C. At present no information is available concerning the rearrangements of atomic positions in the solid taking place during the β to α phase change. This lack of information concerning the phase change is probably due to the fact that malonic acid begins to decarboxylate at the temperature required to bring about the phase change.

As will be shown in Part II, the changes in the infrared spectrum attributed by Amakasu and Ito¹ to the β to α phase change are more likely due to the occurrence of a double-decomposition reaction between malonic acid and the alkali halide used.

In order to understand better some of the changes taking place in the infrared spectrum of malonic acid upon heating the compound, a complete assignment of the infrared absorption bands of crystalline malonic acid was undertaken.

The earliest reference found to the vibrational spectrum of malonic acid was a presentation of the Raman scattering frequencies.³ A more recent Raman spectrum of malonic acid was reported by Ananthanarayanan.⁴ These Raman spectra were obtained from solutions of H₂O saturated with malonic acid (approximately 40% malonic acid by weight). The infrared spectrum of malonic acid from 4000 to 600 K was reported^{5,6} in 1940, along with an accompanying partial band assignment. The most thorough infrared absorption band assignment was one reported by Schmelz et al.⁷ Schmelz et al. also included the assignments for malonic acid-d₄ in their work. More recent reports^{1,8} substantiate the work of Schmelz. No reports dealing with the far infrared spectrum of malonic acid have been found.

Before attempting to assign infrared absorption frequencies to the vibrational motions of a molecule in a crystal, information is needed concerning the structure of the molecule as a single unit and also the structure of the crystal composed of these molecules. An X-ray crystal structure determination⁹ shows malonic acid to consist of long chains of molecules bound together by hydrogen bonded cyclic carboxylic acid dimer units. This structure is depicted in Figure I-1. The dimer chain structure depicted in Figure I-1, for crystalline β -malonic acid means that the planes passing through the acid dimer

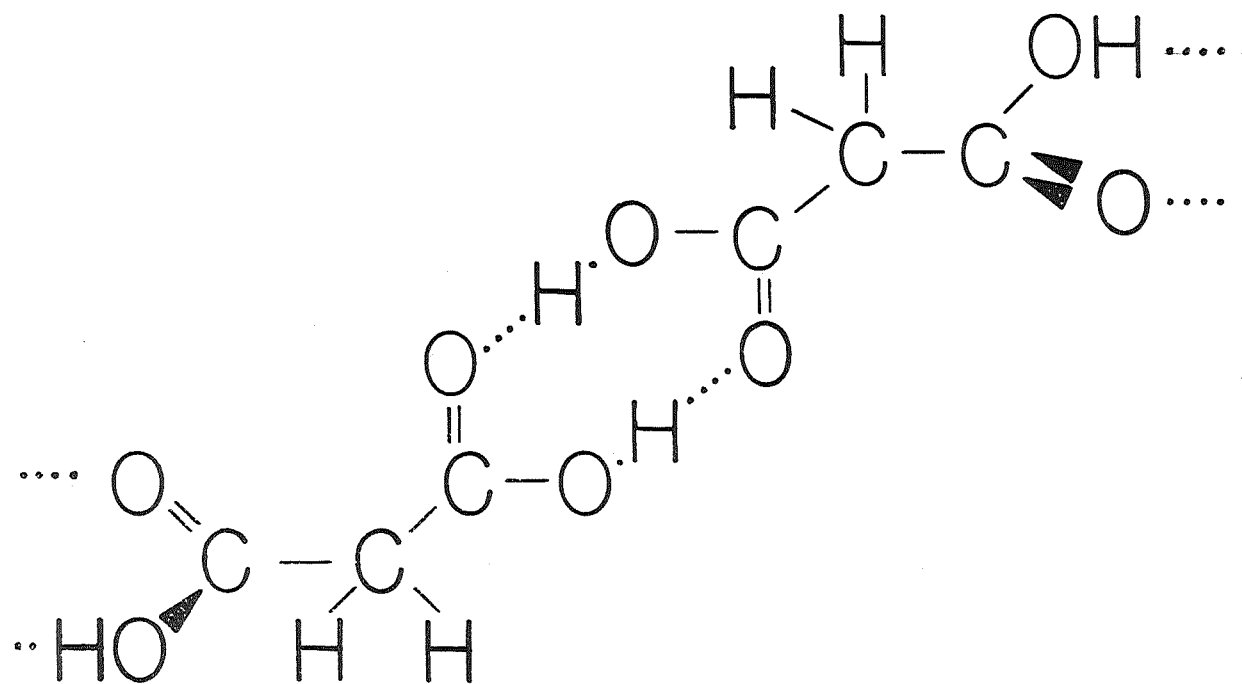


Figure I-1. Representation of the Dimer Structure for β -Malonic Acid.

units at each end of the molecule are almost perpendicular to each other.

I-2: Experimental

Method of Obtaining the Spectrum of Sublimed Malonic Acid

Malonic acid was placed in a 5 cm gas cell fitted with KBr windows. The gas cell was then wrapped with heating tape and the temperature raised to approximately 100° while the pressure in the gas cell was reduced to approximately 0.5 torr. Since the large windows of the gas cell were cooler than the body of the cell, the malonic acid sublimed onto the salt windows. One of the windows was then removed, placed in an infrared spectrophotometer, and the spectrum recorded from 4000 to approximately 400 K, the cut-off limit of KBr.

Method of Obtaining the Infrared Spectrum of Malonic Acid at Low Temperature

A low temperature cell of conventional design¹⁰ was constructed. Since the cell is evacuated during use, the windows are held in place by the force of atmospheric pressure pushing against a set of O-rings. The outer jacket of the cell was encased in a fiber glass insulating jacket.

Method of Obtaining the Mull Spectra of Malonic Acid

Ground malonic acid was mixed with the mulling agent (Nujol or halocarbon) by grinding in an agate mortar, and the infrared spectrum recorded of the mixture placed between salt plates.

Method of Obtaining Solution Spectra of Malonic Acid

Solutions of malonic acid in acetone, ether and pyridine were prepared and the spectrum recorded in cells of thickness of 0.1 mm.

I-3: Results and Discussion

When using the alkali halide pressed pellet technique of obtaining infrared spectra, it was found that, with the exception of cesium chloride and anhydrous sodium bromide, the initial spectra of crystalline malonic acid were identical in appearance regardless of the salts used as pellet materials. The fact that the frequencies of absorption were essentially invariant upon change of salts indicates that the effect of the salt matrices upon the internal bonding of malonic acid is negligible. Because of this invariability of the spectrum of malonic acid from salt to salt, and since the mull spectra of malonic acid were identical to the alkali halide-malonic acid pressed pellet spectra, the spectra recorded using the pressed pellet technique were used in this work to obtain the frequencies for assignment to atomic motions in malonic acid.

The sublimation technique of obtaining infrared spectra of solids provide a possible check on the validity of spectra obtained by other means. Although the sublimation of a pure solid onto salt windows can introduce complications in the infrared spectra due to orientation effects in the solid, the method does give a spectrum of the pure solid uncluttered by solvent bands. In the case of malonic acid, the spectrum of the sublimate is nearly identical to the spectrum

of malonic acid obtained with the KBr pressed pellet technique. The differences in the spectra obtained by the two methods are differences in relative intensities. The fact that the two spectra are nearly identical adds credence to the postulate that the malonic acid spectra obtained by the pressed pellet technique are valid for use in the spectral band assignments.

Solution spectra of malonic acid are, in this case, of marginal value since solutions of the acid do not have the rigid structure of the solid.

The infrared spectrum of malonic acid is shown in Figure I-2. Since the malonic acid molecule in the crystalline state has C_s symmetry, i.e., no symmetry, it should exhibit $3N-6$, or 27 infrared active fundamental motions. As has been previously mentioned, an X-ray crystal structure determination⁹ has shown crystalline β -malonic acid to consist of long chains of molecules bound together in a head to tail arrangement by the cyclic carboxylic acid dimer units. Thus, crystalline malonic acid is actually composed of chains of acid dimer units alternating with CH_2 groups.

It must be emphasized that the only rigorous method of treating the band assignment of malonic acid is a consideration of the crystal unit cell as a whole and, consequently, of the motions of the atoms in this unit cell. This method is quite cumbersome and very involved, consequently it was abandoned in favor of the simplified divided symmetry treatment described below.

For the spectral assignments in this work, malonic acid is considered to consist of two separate symmetry units. One of these

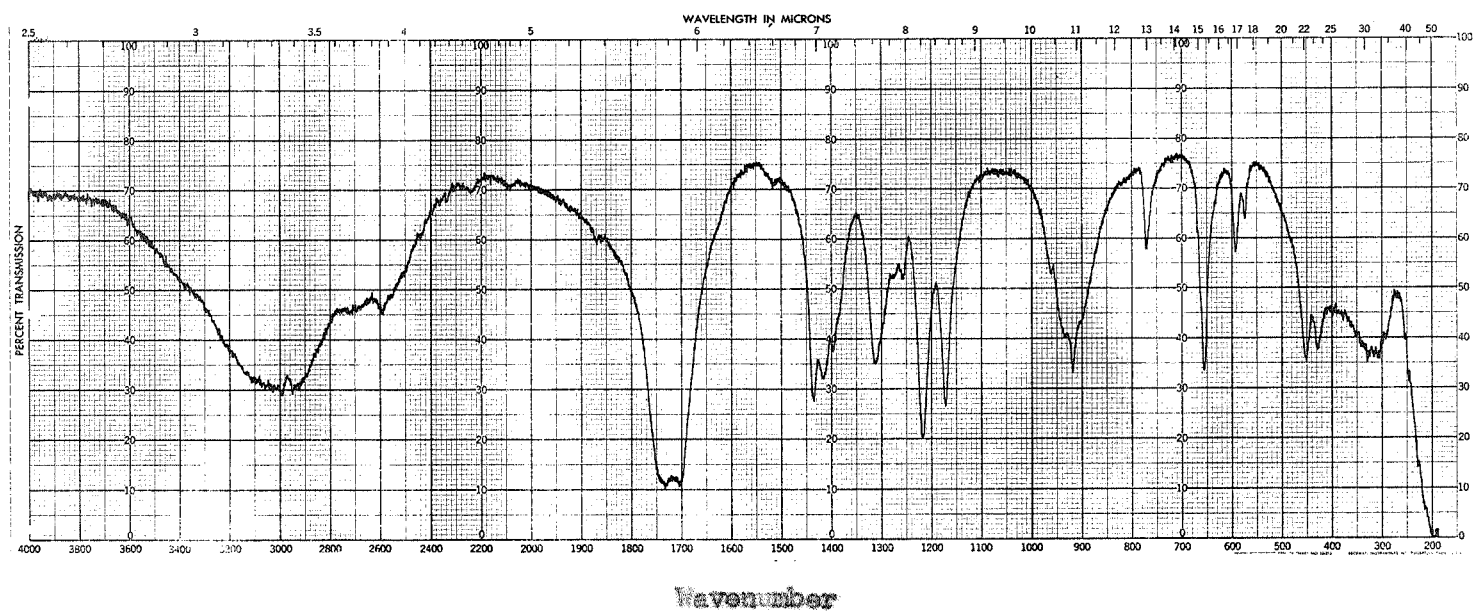


Figure I-2: The Infrared Spectrum of a Pressed Pallet of a Mixture of KBr and Malonic Acid (Approximately 1% Malonic Acid by Weight)

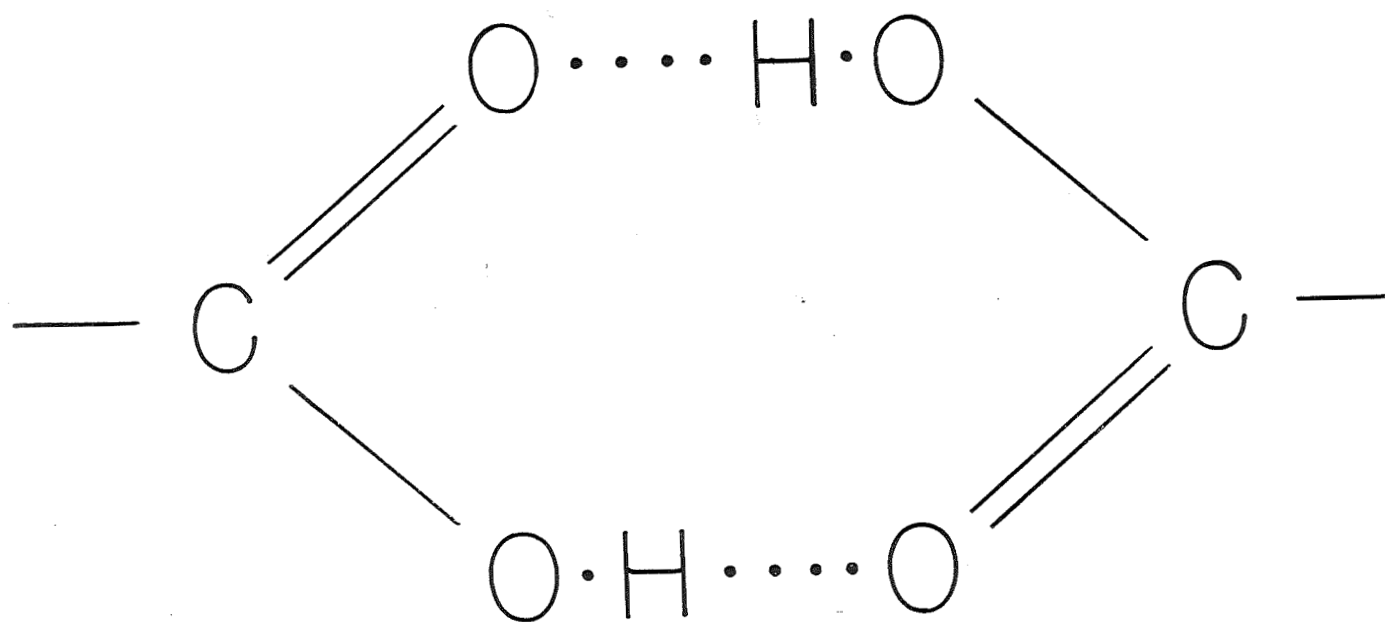


Figure 1-3. The Carboxylic Acid Dimer Structure

units, the cyclic carboxylic acid dimer unit, has the structure shown in Figure I-3. This eight atom planar ring possesses C_{2h} symmetry. The other unit is either a 3-carbon-2 hydrogen skeletal unit with the structure depicted in Figure I-4 or the CH_2 group alone. Both the C_3H_2 unit and the CH_2 units should possess C_{2v} symmetry.

Considering first the dimer unit, this 8 atom ring should possess 18 fundamental vibrational motions. Of these 18 motions, group theory predicts 9 to be infrared active and 9 to be Raman active. Of the 9 infrared active fundamentals, 3 are of A_u symmetry species and 6 are of the B_u symmetry species. Of the 9 Raman active fundamentals, 6 are of the A_g symmetry species and 3 are of the B_g symmetry species. Since the C_{2h} point group possess a center of symmetry, the mutual exclusion principle of Raman and infrared activity is applicable. The 18 fundamental vibrational motions are diagrammed in Figure I-5 as approximate atomic displacements. The figures depicted were derived on a qualitative basis in order to produce motions of the desired symmetry species. The symmetry species of each of the motions are also indicated on Figure I-5.

Considering now the 3 carbon-2 hydrogen skeletal unit, it can be shown that 9 vibrational fundamentals are to be expected for this unit. From these 9 fundamentals belonging to a unit of C_{2v} symmetry, group theory predicts 8 infrared active motions and 9 Raman active motions. The diagram of these fundamental vibrational motions as approximate atomic displacements are shown in Figure I-6 along with the

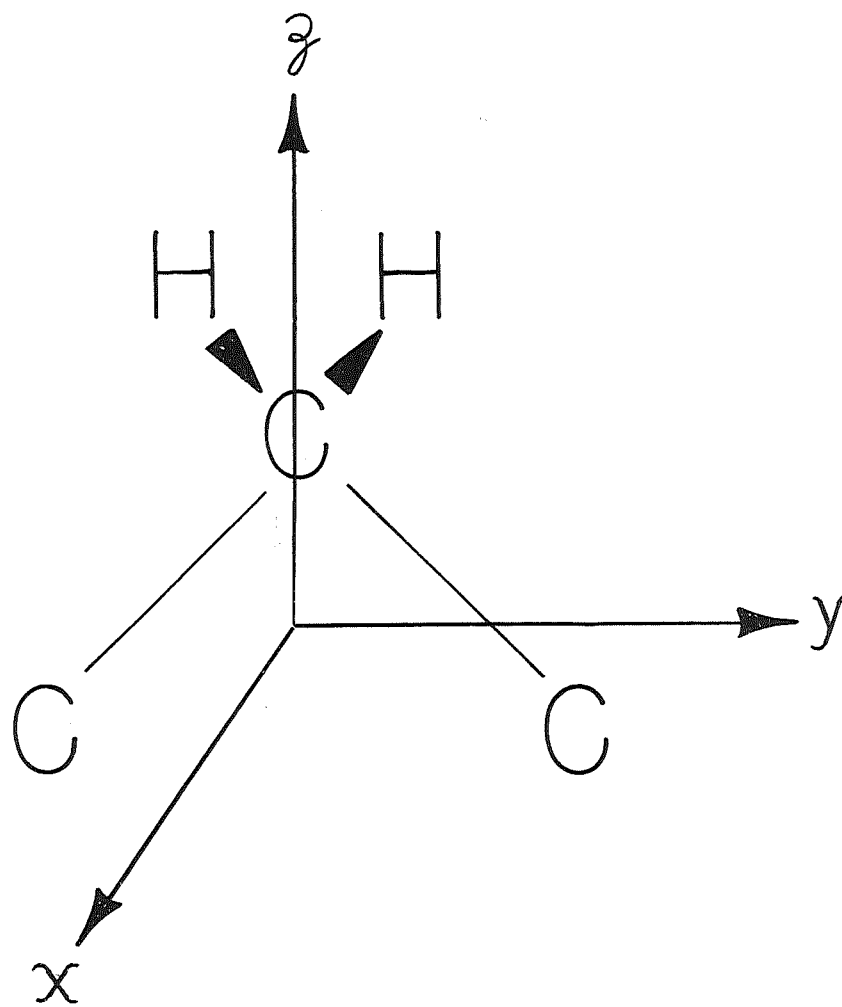


Figure I-4. The Structure of the C_3H_2 Group.

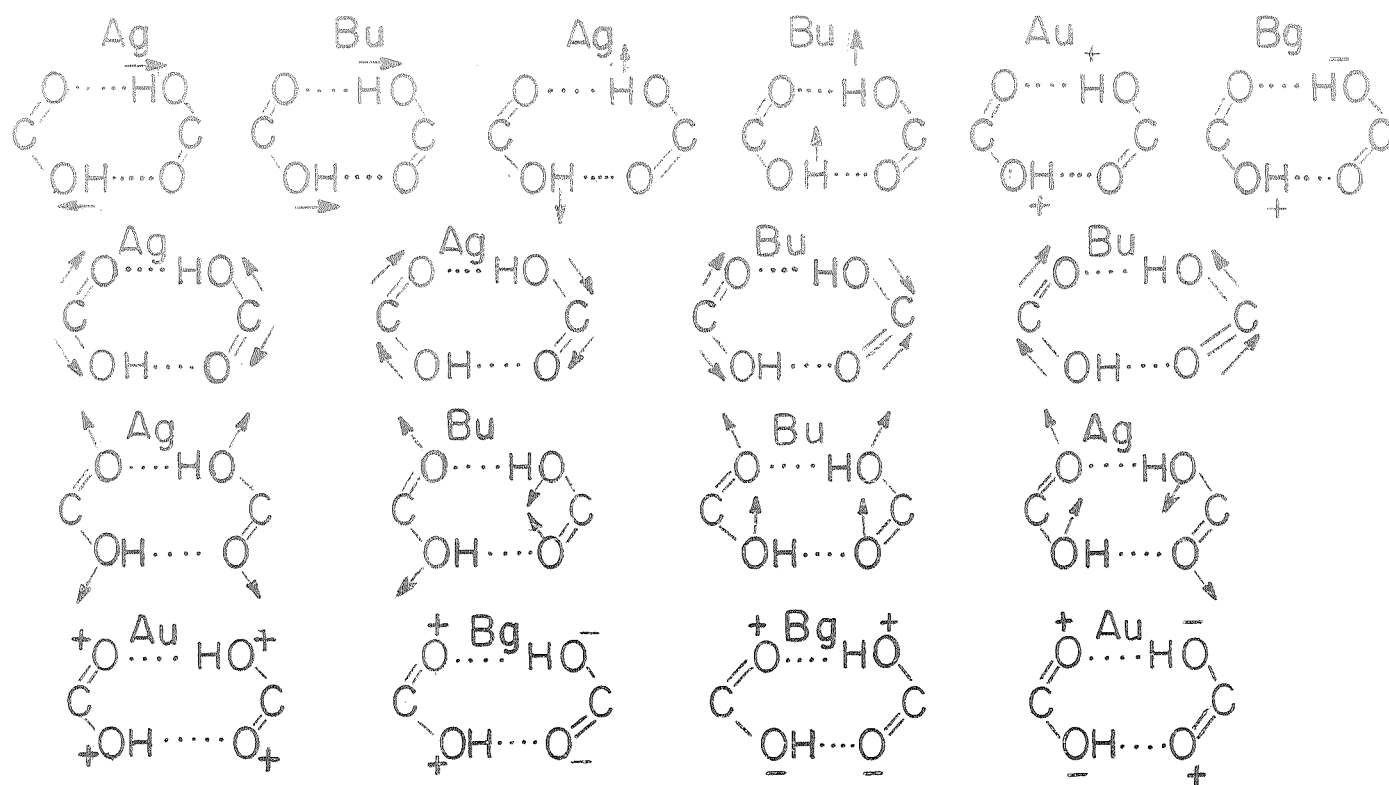


Figure I-5. Atomic Displacements and Symmetry Species for the Fundamental Motions of the $C_2H_2O_4$ Acid Dimer Group of C_{2h} Symmetry.

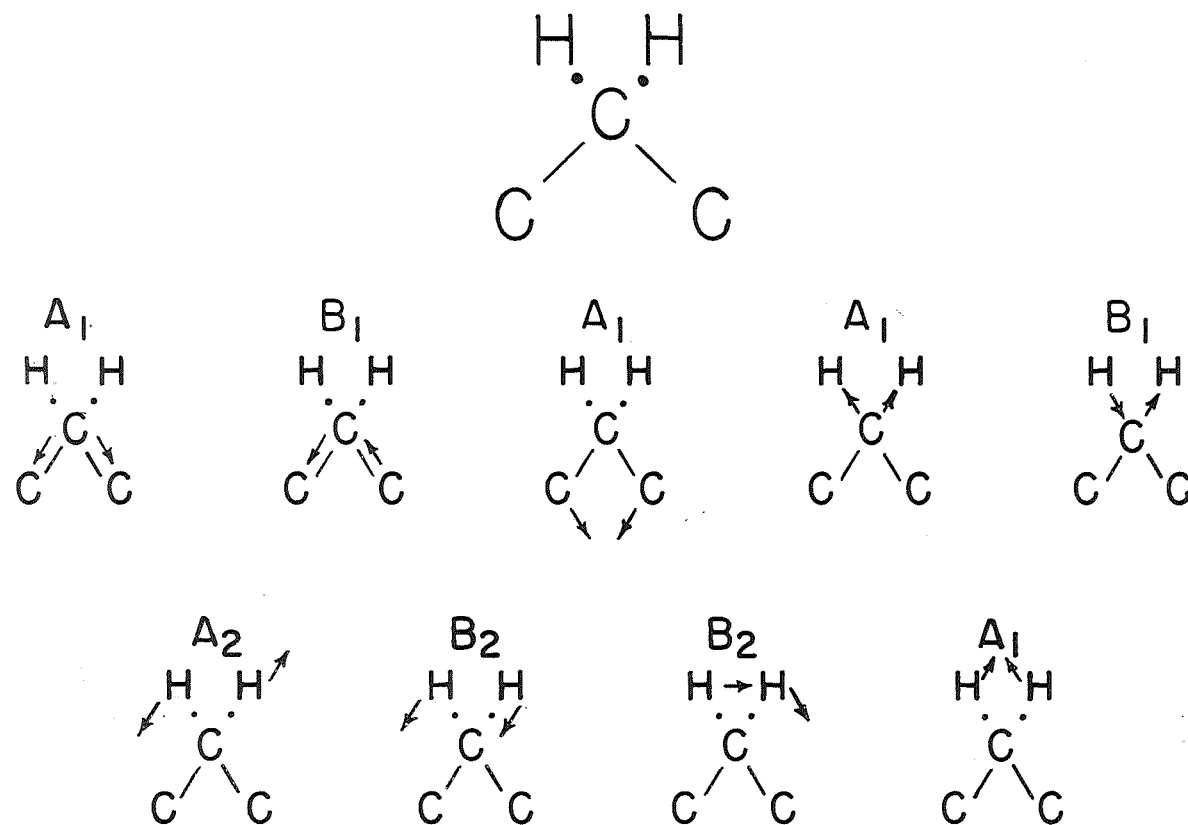


Figure I-6. Atom Displacements and Symmetry Species for a 3-Carbon 2-Hydrogen Skeleton of C_{2v} Symmetry.

corresponding symmetry species of each motion. The motions of the A_1 , B_1 and B_2 symmetry species are infrared active, while the motions of all of the indicated symmetry species are Raman active.

Combining the number of vibrational fundamentals expected for the cyclic dimer unit with those expected for the C_3H_2 group gives a total of 27 fundamental vibrational motions. The fact that this number of fundamentals is the same as that predicted from a consideration of degrees of freedom of the eleven atom malonic acid molecules is due to the use of two of the carbon atoms in both the dimer unit and the skeletal unit.

Another method of considering the fundamental band assignment problem in malonic acid involves the use of the carboxylic acid dimer unit along with the CH_2 group. In this method the assignments for the acid dimer unit remain the same.

The 3 atom CH_2 group should have 3 fundamental vibrational motions and should belong to the C_{2v} point group. The vibrational fundamentals are diagrammed in Figure I-7, as approximate atomic displacements. Along with the three vibrational fundamentals, the 3 translational and 3 rotational degrees of freedom are also shown. This method of assignment involves the postulate that the translational and rotational motions for the CH_2 group can also be assigned frequencies when this group is attached to the rest of the molecule. For instance, the CH_2 translation in the z-direction involves approximately the same atomic displacement as those involved in the C_3H_2 symmetric carbon-carbon stretching motion. Using the same reasoning

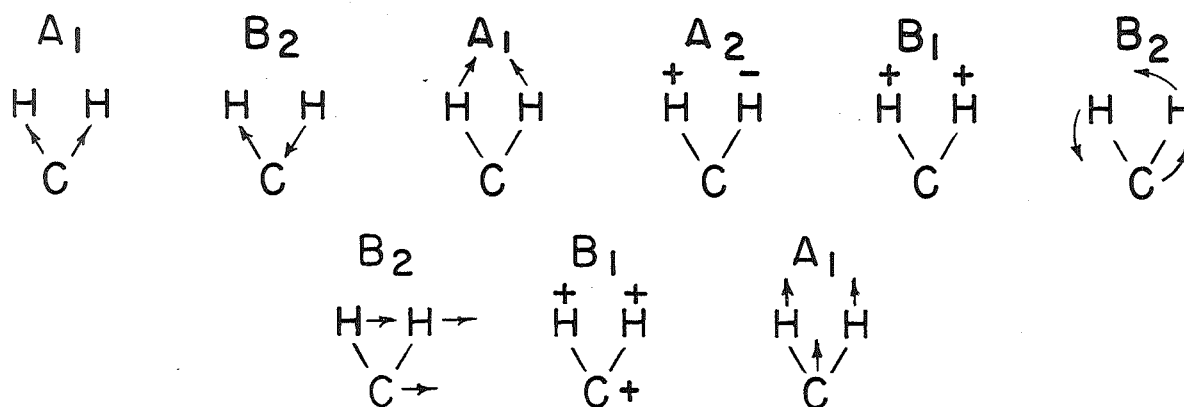
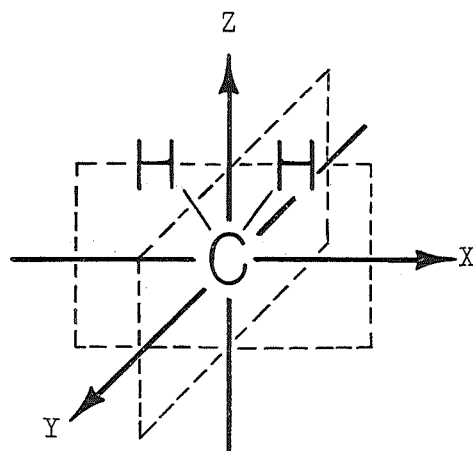


Figure I-7. Atom Displacements, Group Rotations, Group Translations and Symmetry Species for the CH_2 Group of C_{2v} Symmetry.

the CH_2 translation in the y-direction can be considered as the asymmetric stretching motion of the three carbon skeleton. The CH_2 translation in the x-direction would produce a motion analogous to a wagging of the three carbon skeleton.

The same type of treatment can be applied to the rotational motions of the CH_2 units. The rotations of the CH_2 unit around the x, y, and z-axes involve approximately the same atomic motions as those produced by the CH_2 rock, wag, and twist, respectively. The two CH_2 stretching motions and one CH_2 deformation motion remain as before.

The use of the CH_2 group rather than the C_3H_2 group introduces no changes in the infrared and Raman activity.

The absorption band assignments for β -malonic acid (h_4 and d_4) are shown in Table I-1. The ratio of the frequency of a motion including a hydrogen, to the frequency the same motion involving a deuterium provides a check upon the validity of the assignment of a frequency. This ratio should be approximately 1.3 for motions involving a carbon and a hydrogen. The ratios of these motions are shown in Table I-1 wherever applicable.

The Raman data shown in Table I-1 were obtained using a Cary Model 81 Laser Raman Spectrophotometer through the courtesy of J. W. Brasch at the Center for Materials Research, University of Maryland. It can be seen that the Raman and infrared frequencies agree quite well with the exception of the band involving the coupled O-H deformation + C-O stretch + C=O stretch.

Table I-1 shows four bands unassigned. Of these four bands, all are either shoulders on more intense bands or are of low absorption.

TABLE I-1

Assignments of Observed Infrared and Raman Absorption Frequencies for Malonic Acid (d_4 and h_4)

$H_4C_3O_4$	Infrared (K) $D_4C_3O_4$	Ratio H/D	Raman (K) $H_4C_3O_4$	Assignment	
3000	2270	1.32	----	O-H----	Assignment Stretch
Inact	Inact	----	2993	O-H----	Symmetric Stretch
2970	2180	1.33	Inact	CH	Asymmetric Stretch
2920	2180	1.30	2952	CH	Symmetric Stretch
Inact	Inact	----	1685	C=O	Stretch + C-O Stretch
Inact	Inact	----	1660	C=O	Stretch + C-O Stretch
1740	1740	----	Inact	C=O	Stretch + C-O Stretch
1710	1700	----	Inact	C=O	Stretch + C-O Stretch
1440	1100	1.31	Inact	O-H	Deformation + CO + C=O
Inact	Inact	----	?	O-H	Deformation + CO + C=O
1420	1049	1.33	1425	CH ₂	Deformation
1400	----	----	1404	Unassigned	
1360	----	----	----	Unassigned	
1310	1370	----	1325	C-O	Stretch + C=O Stretch + OH
1280	1031	1.22	1285	CH ₂	Twist
1260	----	----	----	Unassigned	

TABLE I-1 (Continued)

Assignments of Observed Infrared and Raman Absorption Frequencies for Malonic Acid (d_4 and h_4)

$H_4C_3O_4$	Infrared (K) $D_4C_3O_4$	Ratio H/D	Raman (K) $H_4C_3O_4$	Assignment	
1220	1056	1.19	1253	CH_3	Wag
1173	1290	----	1180	C-C-C	Asymmetric Stretch
963	935	----	960	C-C-C	Symmetric Stretch
934	750	1.25	Inact	O-H----O	Deformation Asymmetric
Inact	Inact	----	939	C-H----O	Deformation Symmetric
920	670	1.37	922	CH_2	Rock
902	----	----	907	Unassigned	
771	790	----	Inact	O-C=O	Asymmetric In - Plane Deformation
Inact	Inact	----	766	O-C=O	Symmetric In - Plane Deformation
656	600	----	Inact	O-C=O	Symmetric Rock
Inact	Inact	----	642	O-C=O	Asymmetric Rock
591	560	----	Inact	O-C=O	Symmetric Wag
Inact	Inact	----	602	O-C=O	Asymmetric Wag
574	450	----	Inact	O-C=O	Asymmetric Twist
Inact	Inact	----	580	O-C=O	Symmetric Twist
451	417	----	----	C-C-C	Deformation
429	388	----	----	Skeletal Twist	

These bands are probably overtone or combination bands. No attempt was made to give these bands overtone or combination band assignments.

There is a band at 429 K which has been assigned to a skeletal twisting motion. A band in the Raman spectrum of a 40% H_2O solution of malonic acid was also assigned⁴ to the same motion. This motion can also be assigned on the basis of the divided symmetry treatment. The atomic displacements involved in this twisting motion are approximately the same as those involved in a rotation of the 3 carbon 2-hydrogen framework about the z-axis. This motion is of the A_2 symmetry species, however, and should be infrared inactive.

A band at 1280 K has been assigned to the CH_2 twisting motion. This motion is of the A_2 symmetry species and should, therefore, be infrared inactive. However, due to the unsymmetrical nature of the crystalline malonic acid molecule as a unit, this motion could become infrared active.

Figure I-2 shows that the $\text{C}=\text{O}$ stretching frequency (the strong absorption band between 1700 K and 1750 K) is split into a doublet. This splitting is probably due to coupling between the two carbonyl groups at each end of the molecule. This explanation of the splitting is substantiated by the fact that oxalic acid also shows the splitting while dicarboxylic acids with more than one carbon between the carbonyl groups do not show the splitting. This splitting has also been observed¹¹ in the case of diethyl malonate.

Due to the broad diffuse nature of the infrared absorption band arising from the O-H stretching motion occurring at approximately 3000 K all other bands occurring in this region are obscured. The frequencies

listed in Table I-1 for the CH symmetric and asymmetric stretches are taken from the spectrum of dipotassium malonate hydrate (Figure II-13). Although the frequencies of absorption are slightly shifted from one molecule to another it is useful that bands which can be assigned to the symmetric and asymmetric CH stretches are observed in the spectrum of dipotassium malonate-hydrate.

Comparison of the spectra of malonic acid obtained at low temperature with those obtained at room temperature shows no significant difference between the spectra. The infrared absorption bands are much sharper in the spectrum of malonic acid at low temperature. The spectrum of malonic acid at low temperature showed two extra bands in the 1400 K region and two extra bands in the 900-1000 K region. However, those bands were of low absorbances and are not included in the spectral assignment due to the lack of information concerning the low temperature phase behavior of malonic acid.

In conclusion, it can be stated that the divided symmetry treatment enabled the assignment of absorption frequencies to molecular motions in more complicated molecules with more ease than other methods. It should be pointed out, however, that the method is far from rigorous and has ease of use as its major virtue. The method, in this case, relieves the researcher from the task of diagramming the 27 fundamentals of an eleven atom molecule of C_s symmetry and replaces it with the use of two units of higher symmetry.

PART I

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PART II

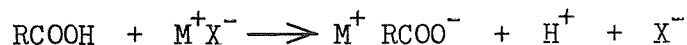
A Study of the Reactions of Malonic Acid With Various Alkali Halide Matrices

II-1: Introduction and Literature Survey

The alkali halide pressed pellet technique has been used extensively for years as a convenient method of obtaining the infrared spectrum of a solid material. When this technique was first introduced^{1,2} a number of investigations were undertaken to study changes in the infrared spectrum of a solid brought about by grinding of the solid with an alkali halide and also to discover what changes, if any, in the infrared spectrum were caused by the high pressures used in the pressing of the pellets. The results of these investigations suggested caution when obtaining infrared spectra by this technique.

Amakasu and Ito^{3,4} have dealt with double decomposition reactions involving organic acids and the alkali halide pellet materials used in pressing the pellets. These double decomposition reactions resulted in the formation of the salt of the acid.

A possible reaction is as follows:



where M^+ = alkali metal ion

X^- = halide ion.

A direct dependence of the double decomposition reaction upon the amount of water present in the pellet material was noted.⁴ For instance,

when oxalic acid was ground with KBr in a constant humidity (40% relative humidity) room and pressed into a pellet, the acid underwent double decomposition with KBr, resulting in the formation of dipotassium oxalate. On the other hand, when oxalic acid was ground with KBr in a dry box and pressed into a pellet the spectra showed that no double decomposition reaction had occurred.

In the present work the findings of Amakasu and Ito^{3,4} have been partially substantiated in regard to double decomposition reactions. No direct correlation was established between the amount of moisture in the pellets and the occurrence of a double decomposition reaction.

When anhydrous NaBr was ground with malonic acid and pressed into a pellet, the infrared spectrum was not the spectrum of β -malonic acid as obtained by mull technique. If NaBr was used as received as the suspension matrix, the resultant spectrum matched the spectrum of β -malonic acid obtained by the mull technique. These observations would tend to indicate a direct correlation between the amount of water present in the pellet and the appearance of the infrared spectrum obtained for malonic acid in the pellet. Such a correlation could not be verified, however. In the case of CsCl an anomalous behavior occurred both in anhydrous (as received) CsCl and in CsCl to which H₂O had been intentionally added.

Actually, malonic acid was found to exhibit the following three different types of behavior in the salts used in this work.

Reaction I: "Normal" decarboxylation (i.e., thermal decarboxylation of malonic acid to acetic acid and carbon dioxide) followed by exchange of the proton of acetic acid with the matrix cation, forming the corresponding acetate salt.

Reaction II: A series of double decomposition reactions involving successive exchanges of protons and the alkali metal cation. This series is terminated with the formation of anhydrous dipotassium malonate.

Reaction III: Anomalous behavior occurring during grinding and/or pressing of the pellets. This reaction occurs only in CsCl and anhydrous NaBr. Unlike Reactions I and II, this reaction requires no heating for occurrence.

The extent and nature of these reactions will be discussed more extensively later.

II-2: Results and Discussion

The first of the three types of behavior that malonic acid exhibits when suspended in alkali halide matrices, is illustrated by the spectra shown in Figures II-1 through II-3. Figure II-1 shows the spectrum of an initial unheated pellet of KBr containing malonic acid. This spectrum is identical to the initial spectra obtained in all of the salts studied in the work except in CsCl and in anhydrous NaBr. The first change occurring in the infrared spectrum of the pellet upon heating a KBr-malonic acid pellet is evident by comparing Figure II-1 with

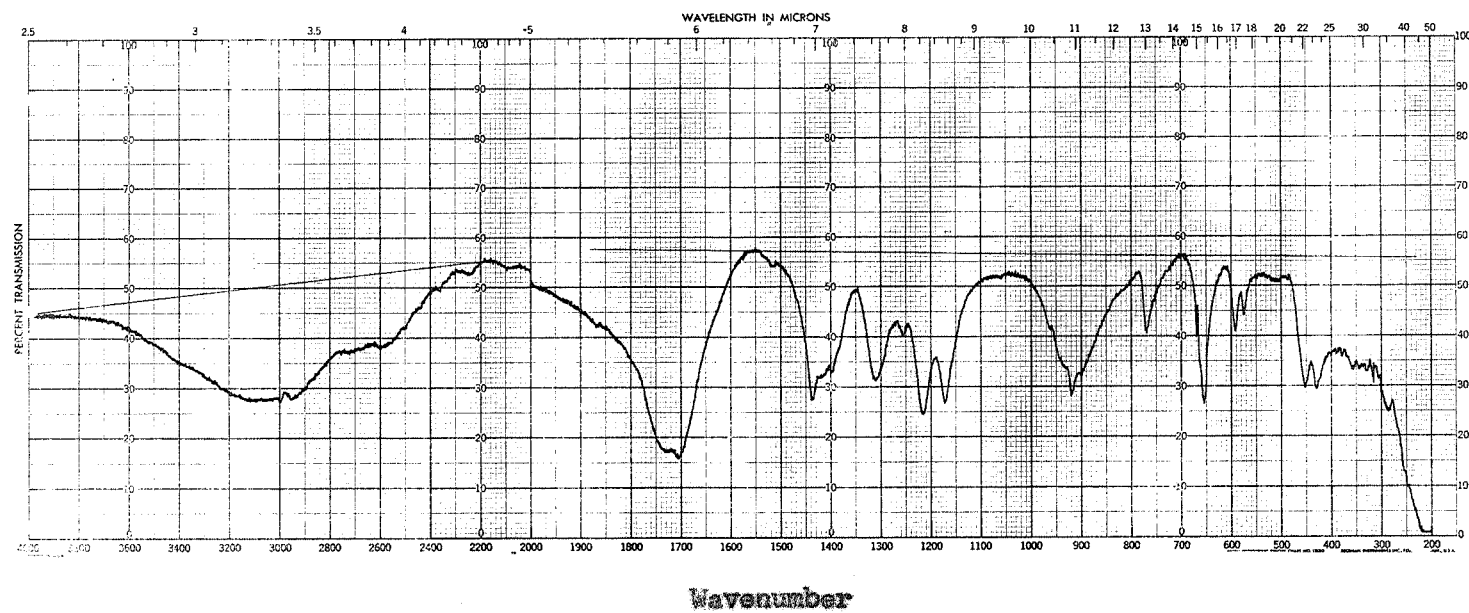


Figure II-1: Infrared Spectrum of a Pressed Pellet of KBr-Malonic Acid (Approximately .5% Malonic Acid by Weight)

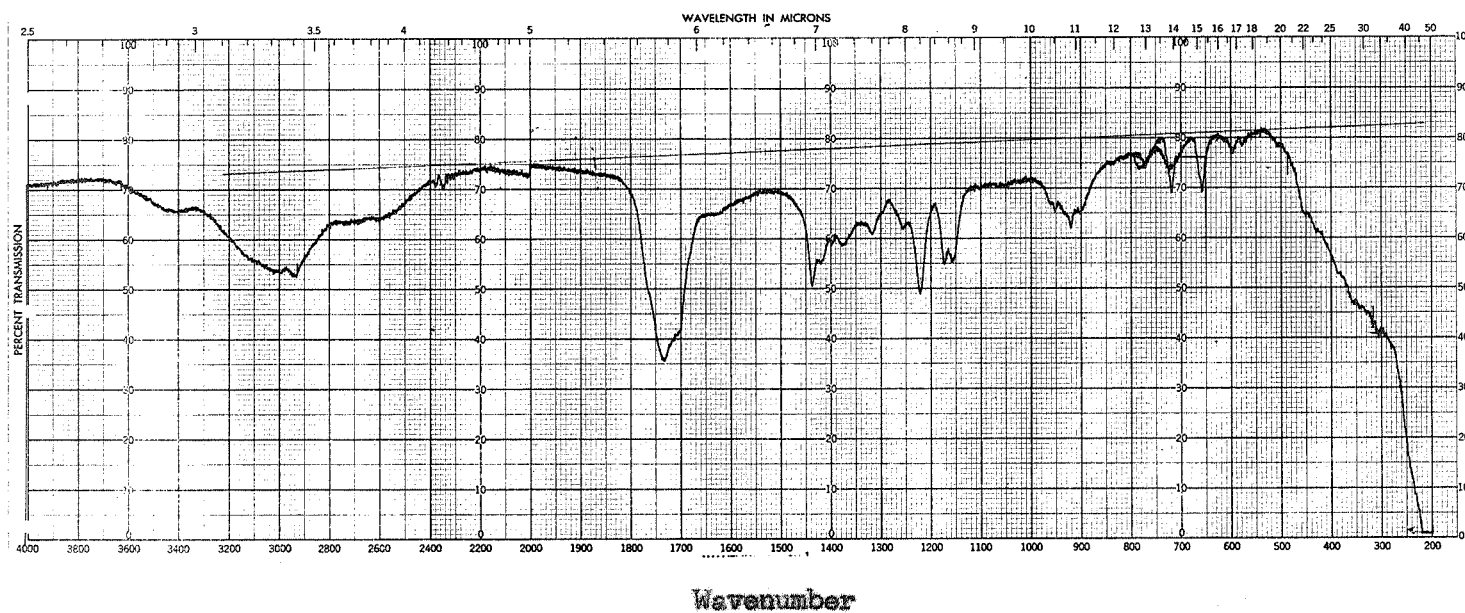


Figure II-2: Infrared Spectrum of a Pressed Pellet of KBr-Malonic Acid After Heating the Pellet for 8.5 Minutes at 158.1°.

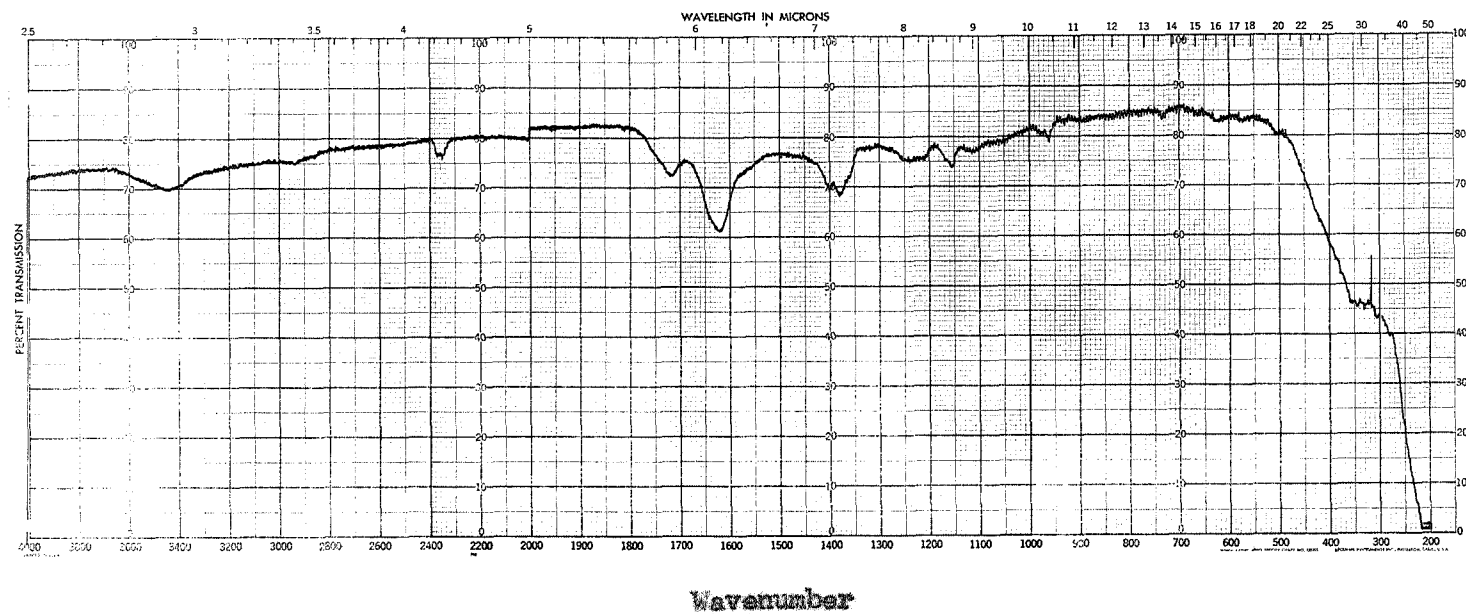


Figure II-3: Infrared Spectrum of a Pressed Pellet of KBr-Malonic Acid After Heating the Pellet for 18.5 Minutes at 158.1° .

Figure II-2. Although the changes in the spectrum are subtle, they are, nevertheless, real. These changes are not well understood at this time. The second change is a gradual disappearance of the major absorption bands due to the decarboxylation of the malonic acid. The acetic acid is partially vaporized at the temperature used (158°) and, upon diffusing out of the pellet, produces a noticeable odor of acetic acid in the reaction tubes. Production of CO_2 can be verified by the appearance of an infrared absorption band at 2360 (K) which is due to the asymmetric $\text{O}=\text{C}=\text{O}$ stretching motion. Figure II-3 shows the infrared spectrum of a KBr pellet after thermal decarboxylation of the malonic acid contained in the pellet has taken place. The major bands observed in the spectrum of the pellet are due to the acetate ion, a small amount of which forms by way of a double decomposition reaction between acetic acid and the KBr matrix material. The other products of the double decomposition reaction (H^+ and Br^- ions in this case) are not observed in the pellets. Some possible reasons for not observing this product will be discussed later.

The second type of behavior observed during application of heat to alkali halide-malonic acid pellets, is best illustrated by the KCl-malonic acid system. The spectra shown in Figures II-4 through II-8 depict the changes which occur in this system upon application of heat. Figure II-4 shows the initial infrared spectrum of malonic acid suspended in a KCl matrix. It can be seen that Figure II-1 and II-4 are nearly identical. Figure II-5 shows the spectrum of potassium hydrogen dimonohydrogen malonate, KH(MHM)_2 , which forms in pellets of KCl, containing malonic acid, after approximately 5 minutes of heating at 140° . It is

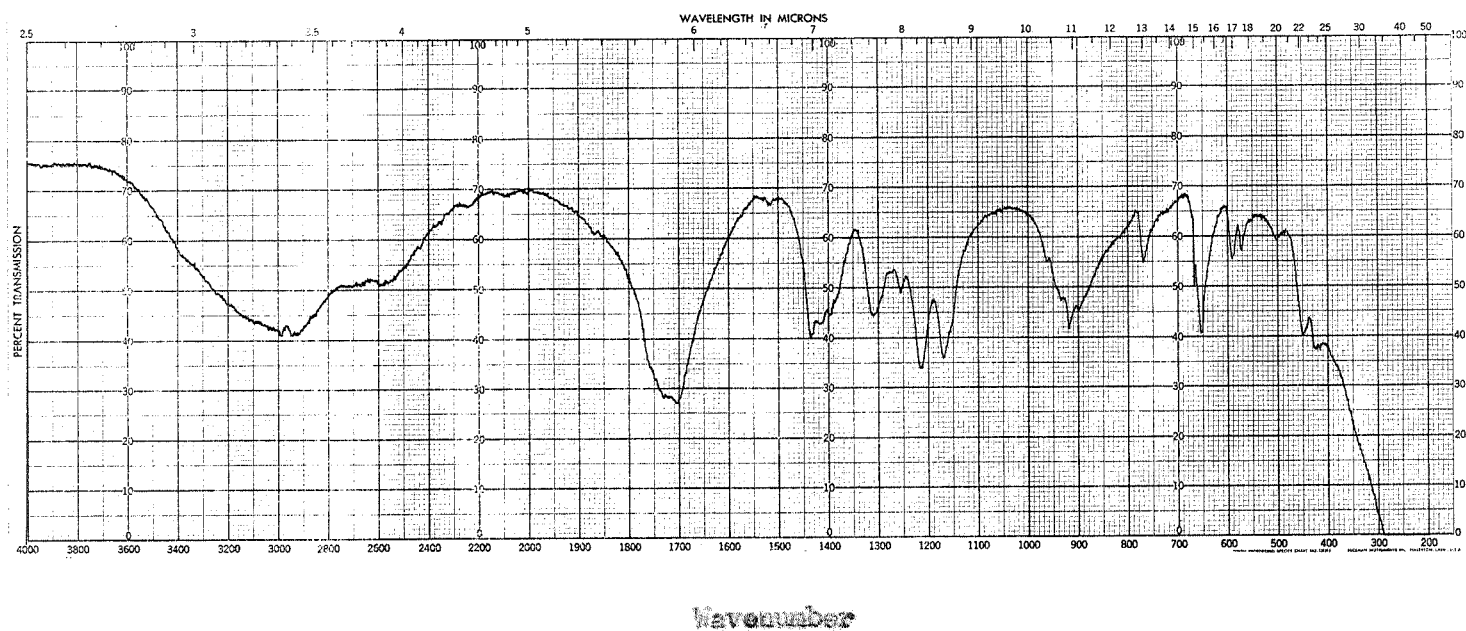


Figure II-4: Infrared Spectrum of a Pressed Pellet of KCl-Malonic Acid (Approximately .5% Malonic Acid by Weight)

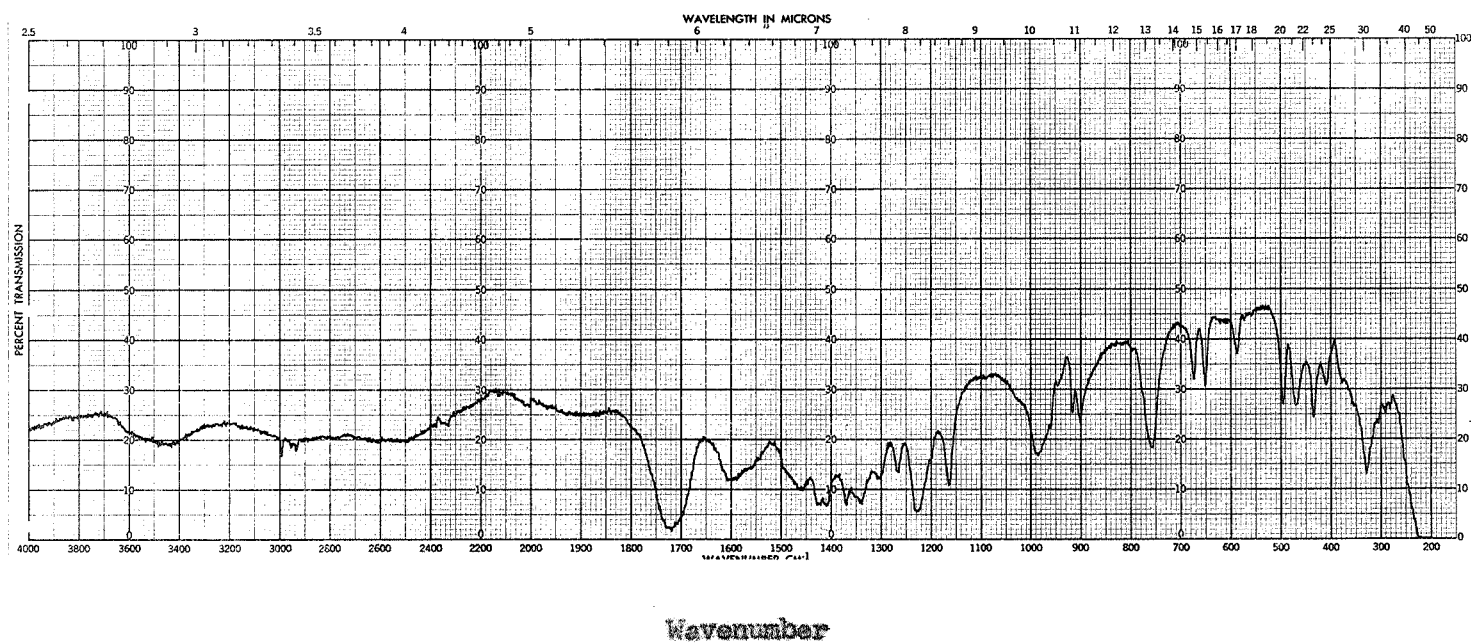


Figure II-5: Infrared Spectrum of a Pressed Pellet of KCl-Malonic Acid After Heating the Pressed Pellet for 1 Minute at 160.7°.

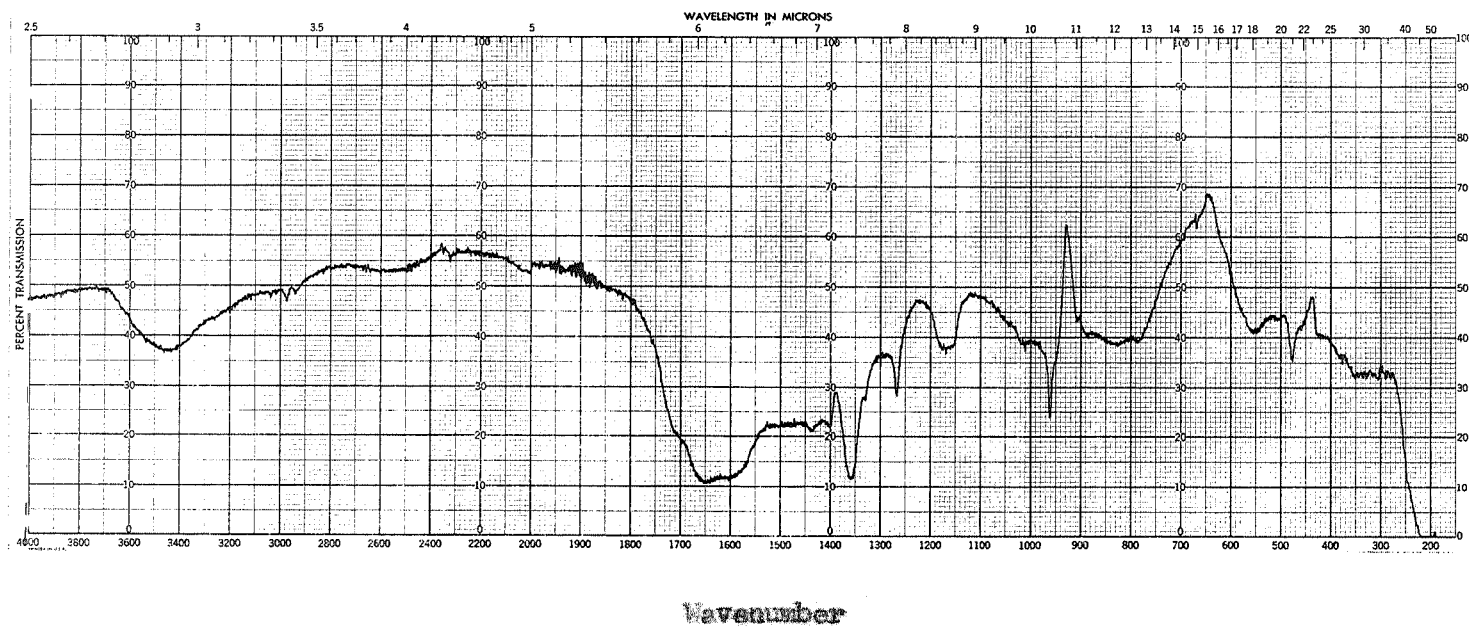


Figure II-6: Infrared Spectrum of a Pressed Pellet of KCl-Malonic Acid After Heating the Pellet for 4.5 Minutes at 160.7°.

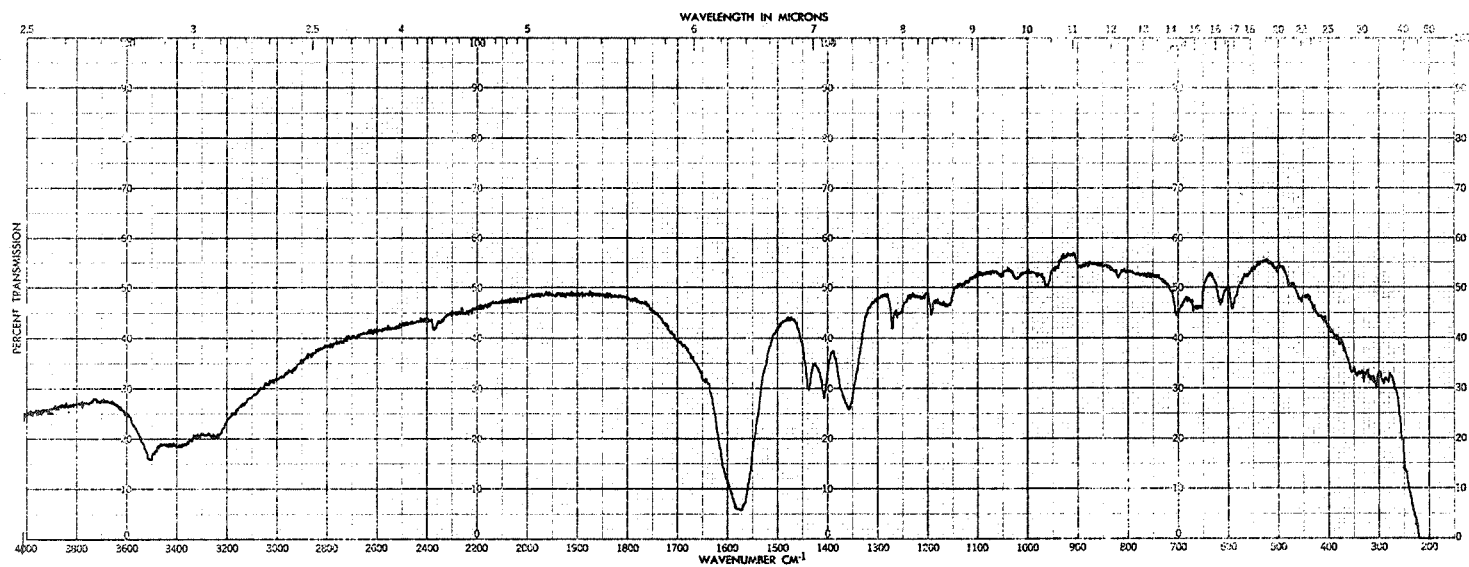
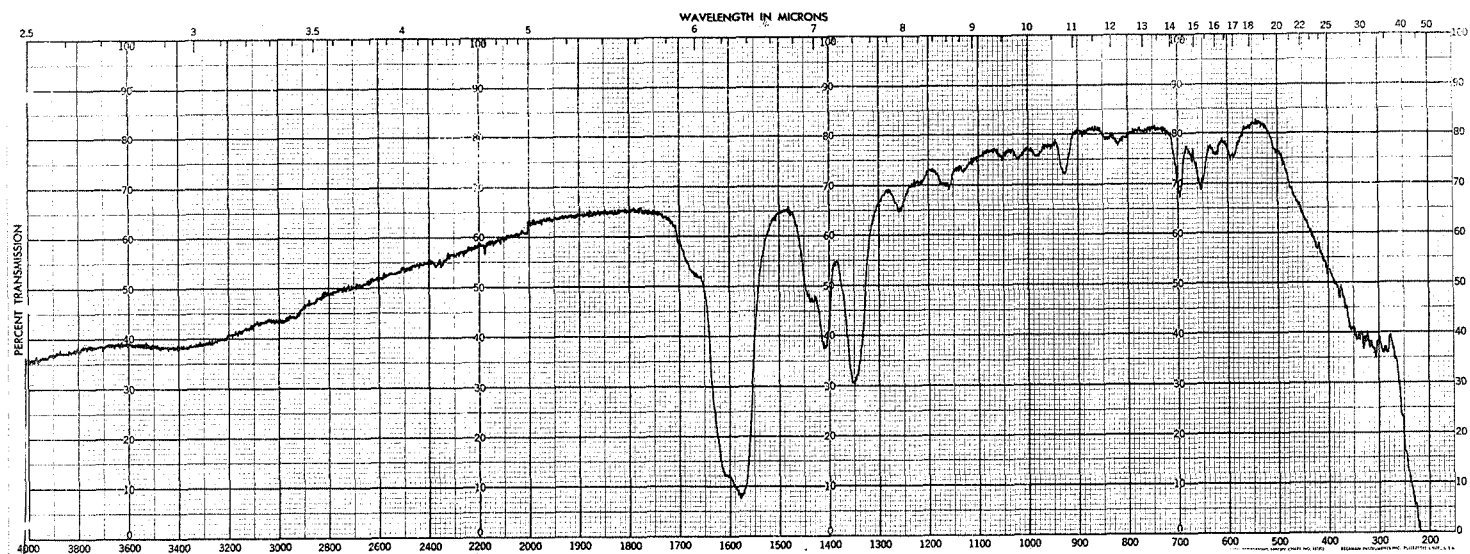


Figure II-7[†] Infrared Spectrum of a Pressed Pellet of KCl-Malonic Acid After Heating the Pellet for 25 Minutes at 160.7°.



Wavenumber

Figure II-8: Infrared Spectrum of a Pressed Pellet of KCl-Malonic Acid After Heating the Pellet for 21.5 Hours at 160.7°.

this change to KH(MHM)_2 which was erroneously attributed to a change from β -to α -malonic acid by Amakasu and Ito.³ The spectrum shown in Figure II-5 can be seen to match the spectrum shown in Figure II-9, which is the spectrum of an authentic sample of KH(MHM)_2 .

One method of preparing KH(MHM)_2 involves mixing malonic acid and KOH in a 2:1 ratio in H_2O and evaporating the H_2O by reduced pressure. This method of preparation is described in Section II-3-2 and results in a relatively pure, crystalline product. It should be noted, however, that, as shown in Fig. II-10 the product resulting from a mixture of malonic acid and KOH in a 1.5:1 mole ratio possesses practically the same infrared spectrum as the product obtained from mixing malonic acid and KOH in a 2:1 mole ratio.

Another method of preparation of KH(MHM)_2 (see Section II-1-2) involves precipitation of KH(MHM)_2 from an acetone or ethanol solution of malonic acid by addition of solid KOH to the solution.

A possible explanation for the formation of KH(MHM)_2 can be advanced by considering the structure of crystalline malonic acid. As was discussed in the General Introduction and Experimental Section, crystalline malonic acid consists of long chains of intramolecularly hydrogen bonded molecules. Insertion of a potassium ion, and removal of a proton, in every other one of the cyclic dimer units would produce a material of molecular formula $\text{KC}_6\text{H}_7\text{O}_8$ which corresponds to the formula for KH(MHM)_2 .

Figure II-6 is the spectrum of potassium monohydrogen malonate K(MHM) , which forms upon further heating of a KCl pellet containing

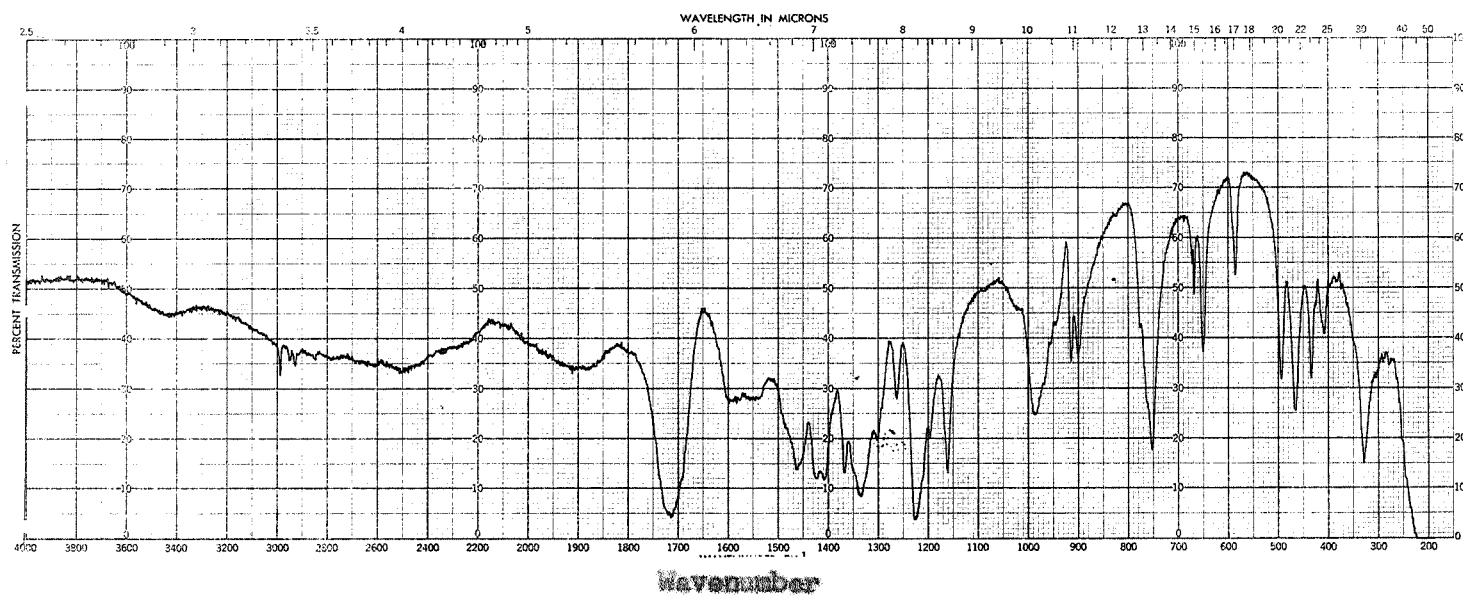


Figure II-9: Infrared Spectrum of the Product Obtained by Evaporation of the Solvent from a Water Solution of KOH and Malonic Acid in a 1:2 Mole Ratio (Spectrum Obtained by the KBr Pressed Pellet Technique)

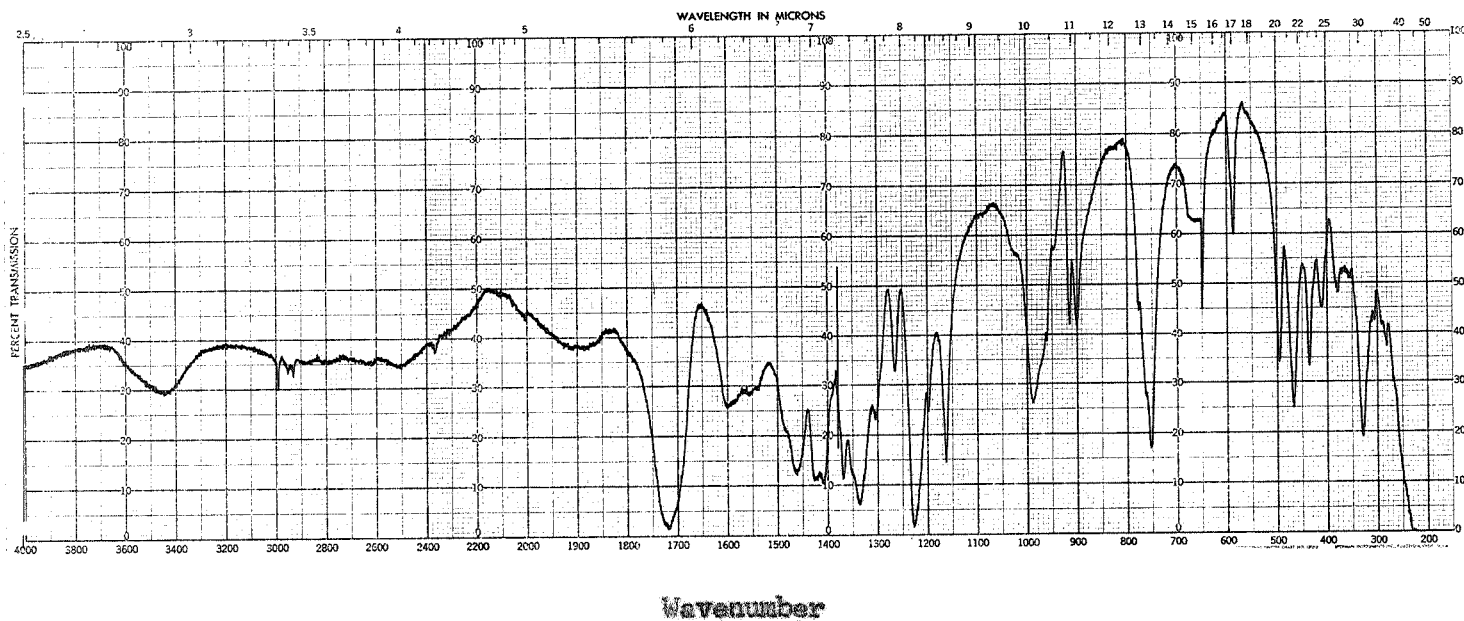


Figure II-10: Infrared Spectrum of the Product Obtained by Evaporation of the Solvent from a Water Solution of KOH and Malonic Acid in a 1:1.5 Mole Ratio (Spectrum Obtained by the KBr Pressed Pellet Technique).

malonic acid. This spectrum may be compared with the spectrum shown in Figure II-11, which is the spectrum of K(MHM). This material was obtained by evaporation of the water from a solution of malonic acid and KOH in a 1:1 mole ratio. K(MHM) is difficult to prepare in a pure form since a crystalline product can be extracted from a solution of any mole ratio of malonic acid to KOH from 2:1 to 1:2. The position of the infrared absorption band due to the carbonyl stretching motion is quite dependent upon the amount of hydrogen bonding present in the molecule, hence, upon the KOH-malonic acid mole ratio. This can be seen by consideration of Figures II-10, II-11 and II-12. In the compounds whose spectra appear in these Figures, the KOH-malonic acid mole ratio varies from 1:1.5 in Figure II-10 to 1.5:1 in Figure II-12. The position of the absorption band due to the carbonyl motion becomes successively higher in frequency as the KOH-malonic acid mole ratio increases.

Figure II-7 shows the spectrum exhibited by an "anhydrous" KCl pellet containing malonic acid after approximately 25 minutes of heating of the pellet at 140° . This spectrum agrees reasonably well with the spectrum (Fig. II-13) of the compound dipotassium malonate-mono-hydrate ($K_2M \cdot H_2O$) which was prepared by evaporation of water from an aqueous solution in which KOH and malonic acid are present in a 2:1 mole ratio, respectively. Inspection of the spectra presented in Figures II-6 and II-11 shows appreciable absorption in the 3400 K region. This absorption is due to the water of hydration, in the $K_2M \cdot H_2O$ molecule.

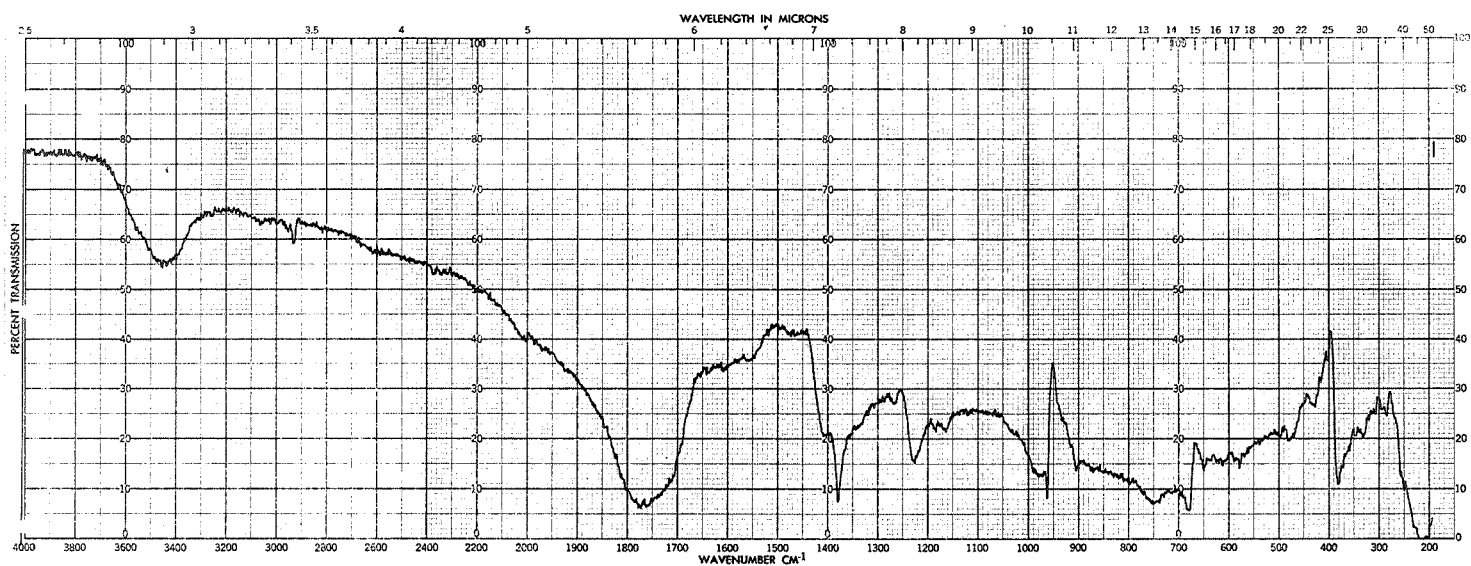


Figure II-11: Infrared Spectrum of the Product Obtained by Evaporation of the Solvent from a Water Solution of KOH and Malonic Acid in a 1:1 Mole Ratio (Spectrum Obtained by the KBr Pressed Pellet Technique).

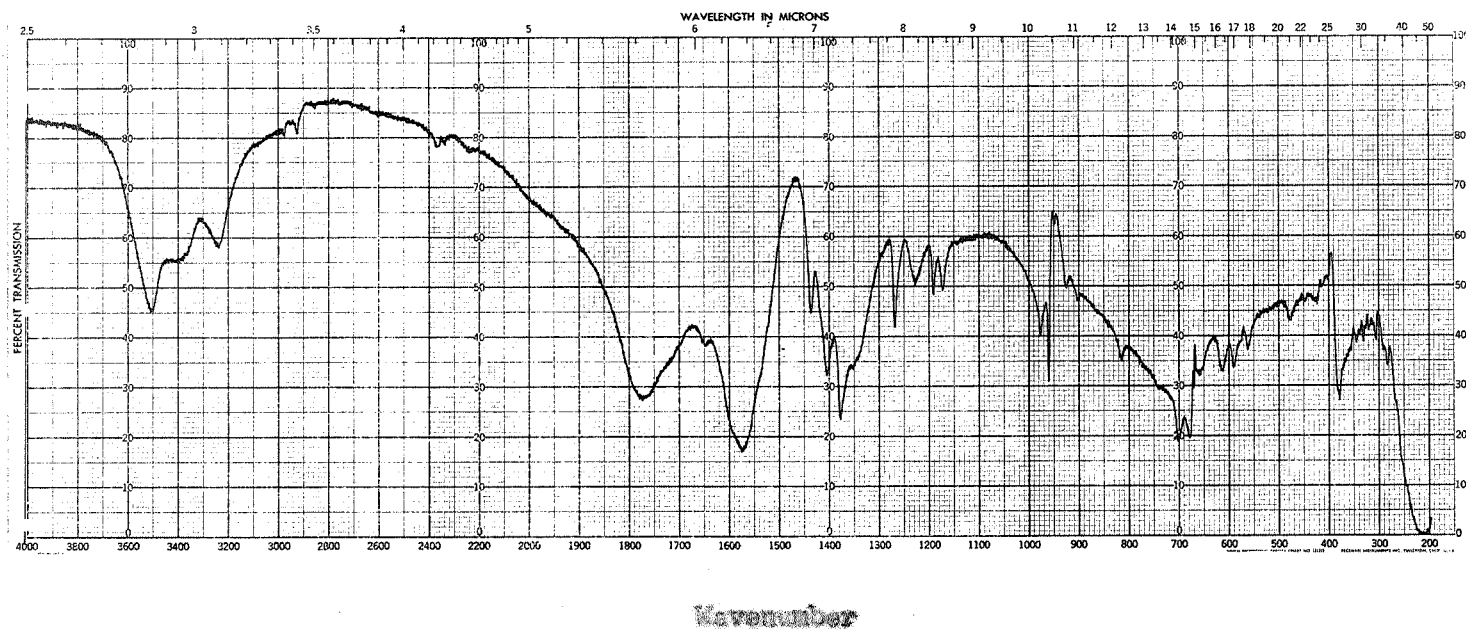


Figure II-12: Infrared Spectrum of the Product Obtained by Evaporation of the Solvent from a Water Solution of KHE and Malonic Acid in a 1.5:1 Mole Ratio (Spectrum Obtained by the KBr Pressed Pellet Technique).

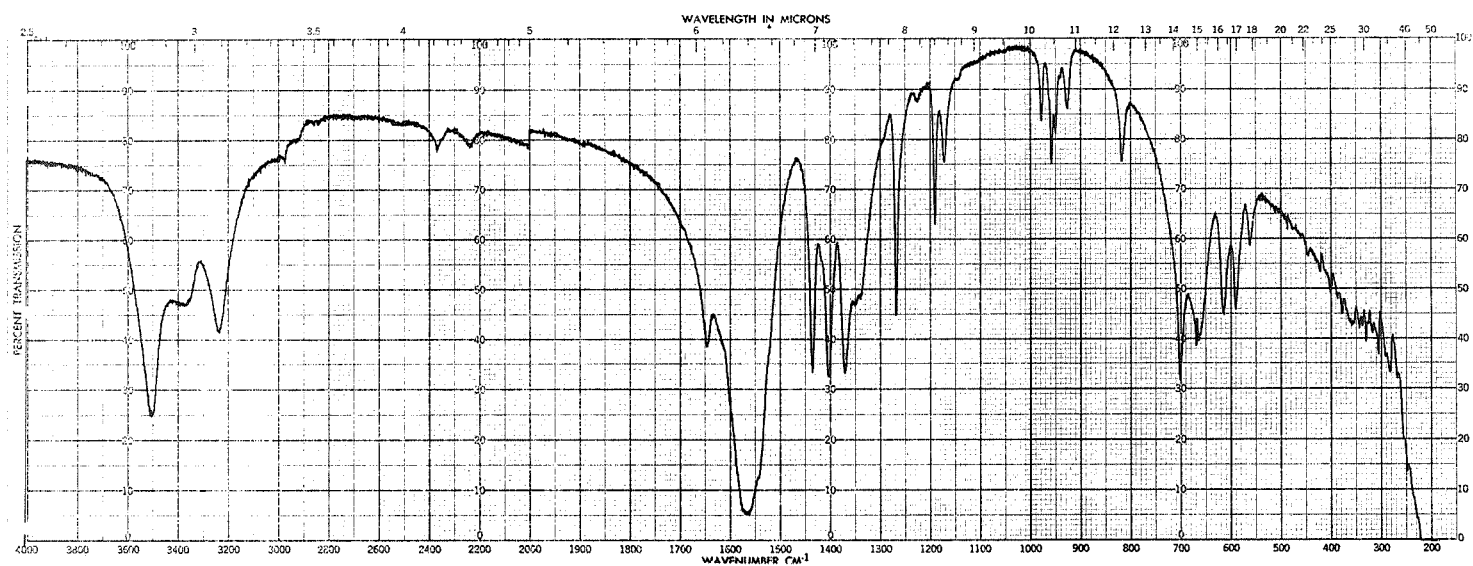


Figure II-13: Infrared Spectrum of the Product Obtained by Evaporation of the Solvent from a Water Solution of KOH and Malonic Acid in a 2:1 Mole Ratio (Spectrum Obtained by the KBr Pressed Pellet Technique).

The formation of an hydrate in supposedly anhydrous materials is at first glance perplexing. However, since the infrared spectrum of the pre-dried starting material (KCl in this case) shows a detectable amount of water to be present, it is possible that the amount of water present is sufficient to produce the monohydrate. An 0.2 gram pellet containing 1% malonic acid by weight would require only 0.00035 gram water or 0.1% H_2O by weight) to produce $K_2M \cdot H_2O$. This highlights the fact that, in the pressed pellet technique, the effect of traces of water can rarely, if ever, be completely ignored.

When hydrated dipotassium malonate is heated under reduced pressure, the water of hydration is removed. The spectrum (Fig. II-14) of partially dehydrated $K_2M \cdot H_2O$ is identical in its major features to the spectrum shown in Fig. II-8. The spectrum shown in Fig. II-14 agrees with that given by Sadtler* as the infrared spectrum of K_2M . The spectrum shown in Fig. II-8 was obtained from a KCl-malonic acid pellet which had been heated at 140° for 40 minutes. Dipotassium malonate-monohydrate can be reproduced by recrystallization of anhydrous dipotassium malonate from water.

Further heating of the KCl-malonic acid pellet produced no other changes in the spectrum from that shown in Fig. II-8, even when the temperature was increased to 180° .

Review of the five steps of the double decomposition reaction for malonic acid and an alkali halide shows that, for each mole of malonic

*Sadtler Standard Infrared Spectrum Number 6204.

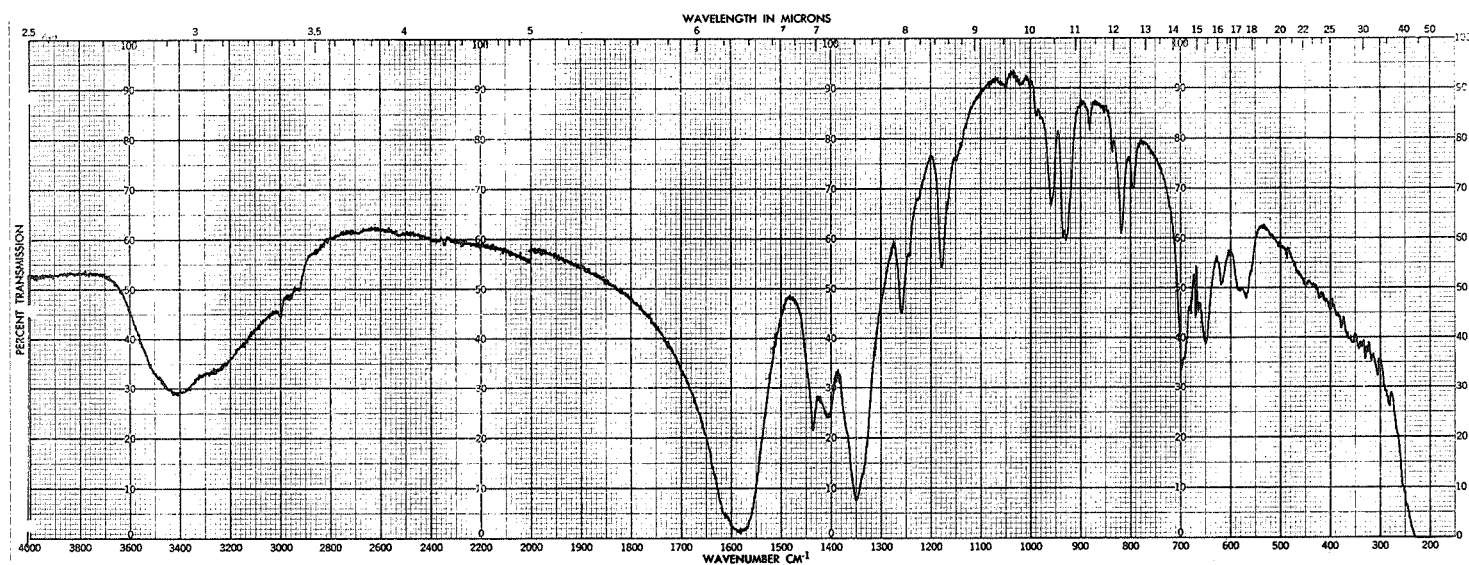


Figure II-14: Infrared Spectrum of Dipotassium Malonate Mono-Hydrate after the Compound Had Been Heated at 200°C Under Reduced Pressure (Approximately .5 Torr) for 1 Hour (Spectrum Obtained by the KBr Pressed Pellet Technique).

acid reacting in an alkali halide, two moles of the corresponding hydrogen halide should be produced. In none of the pellet materials studied were the hydrogen halides detected either during or after occurrence of the double decomposition reaction. No gaseous hydrogen halide was observed even when a mixture of KCl and malonic acid containing a relatively high percentage of malonic acid was heated for a long period of time. Hydrogen halide, trapped in the matrix, was not observed when portions of the same mixture were pressed into pellets and their infrared spectrum obtained.

The fact that the hydrogen halide is not observed in the case of the heated malonic acid-KCl mixtures could mean one, or more, of three things: (1) the HCl produced remains trapped in the pellets and is not observed for some reason, (2) the HCl remains in the pellets as H^+ ions and chloride ions, or (3) experimental conditions were not correct for observing the evolved HCl.

Other work has shown that HCl is observed* above pellets of hydroxylamine hydrochloride, of composition similar to that used for the malonic acid studies when heated in a sealed 10 cm gas cell. Possibly the most reasonable explanation for not observing hydrogen halide in this work is that the hydrogen halide remains trapped in the pellets as H^+ and halide ions.

The third and last of the three types of behavior for malonic acid in alkali halide pressed pellets remains an anomaly. This anomalous behavior occurs in anhydrous NaBr and in both wet and "dry" CsCl. Figures II-15 and II-16 show spectra of the products of the anomalous behavior

*Private communication from Mr. Robert Berkshire, W.V.U. summer undergraduate research student in 1968.

obtained in anhydrous NaBr and "dry" CsCl respectively. The anomalous behavior does not occur, however, in NaBr used as received, indicating a possible dependence of the behavior upon the amount of moisture present in the pellet material. This dependence upon moisture is not borne out, however, in the case of moist CsCl, in which malonic acid still exhibits the anomalous behavior.

Several bits of experimental evidence point to the fact that the product of the anomalous behavior is still some form of malonic acid. One bit of evidence is the fact that strong heating (150°) of a CsCl-malonic acid pellet produces acetic acid and carbon dioxide. Another bit of evidence was obtained from thin layer chromatography (TLC). TLC shows that an acetone solution, obtained by washing a preground malonic acid-CsCl mixture with acetone, contained only one product, the retention time of which was the same as that of malonic acid. The infrared spectrum of a pellet pressed from the same preground CsCl-malonic acid mixture which had been washed with acetone, showed only infrared absorption bands due to water. Still another bit of evidence that the product of the anomalous behavior was malonic acid was the fact that an nmr spectrum of the acetone wash solution from the experiment described above was identical to the nmr spectrum of malonic acid in acetone solution.

Hartman and Hisatsune⁵ observed an effect which they attributed to the formation of a solid solution in their work on the thermal decomposition of calcium formate in alkali halide pressed pellets. They observed that after a heating period of an hour at approximately 100° the infrared spectrum of calcium formate underwent drastic changes. These changes were attributed to solid solution formation. It is possible that the anomalous behavior shown by malonic acid in CsCl and anhydrous NaBr is a solid solution formation which is occurring at lower temperatures. It is not understood, at the present time, why this behavior is not exhibited by all of the salts studied.

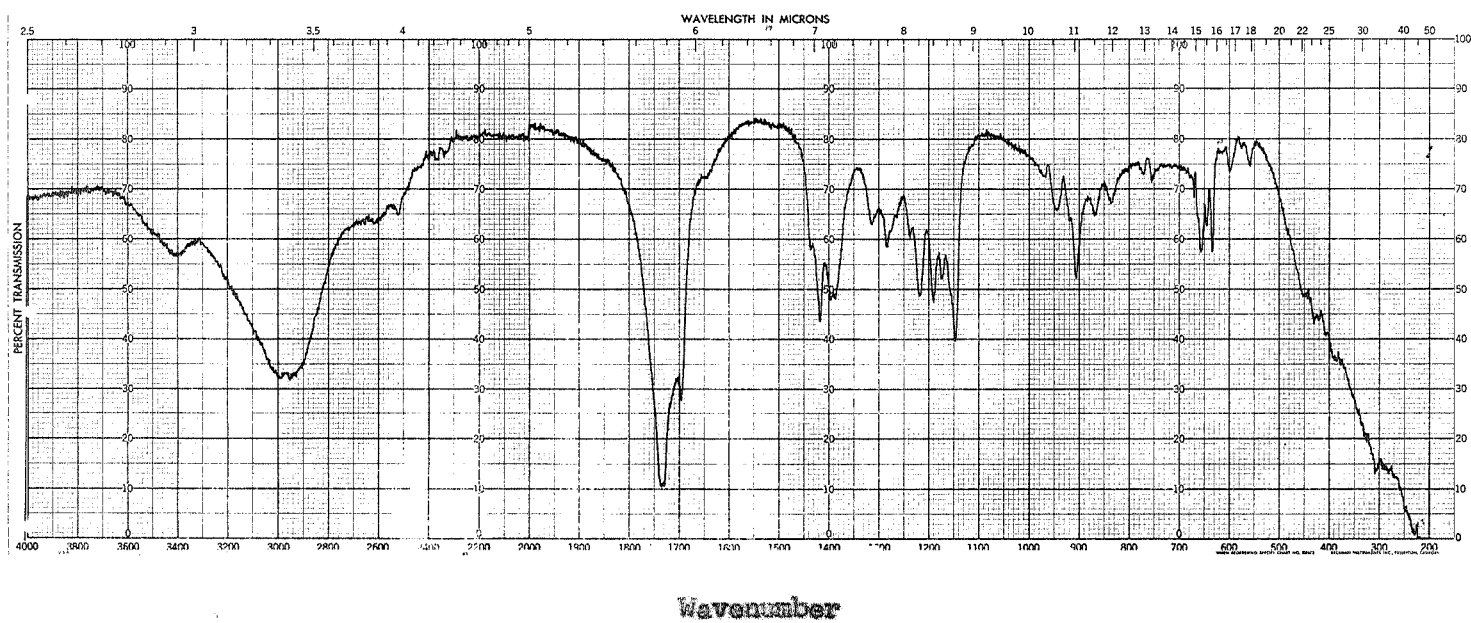


Figure II-15. Infrared Spectrum of a Pressed Pellet of Malonic Acid and Anhydrous NaBr Ground Together.

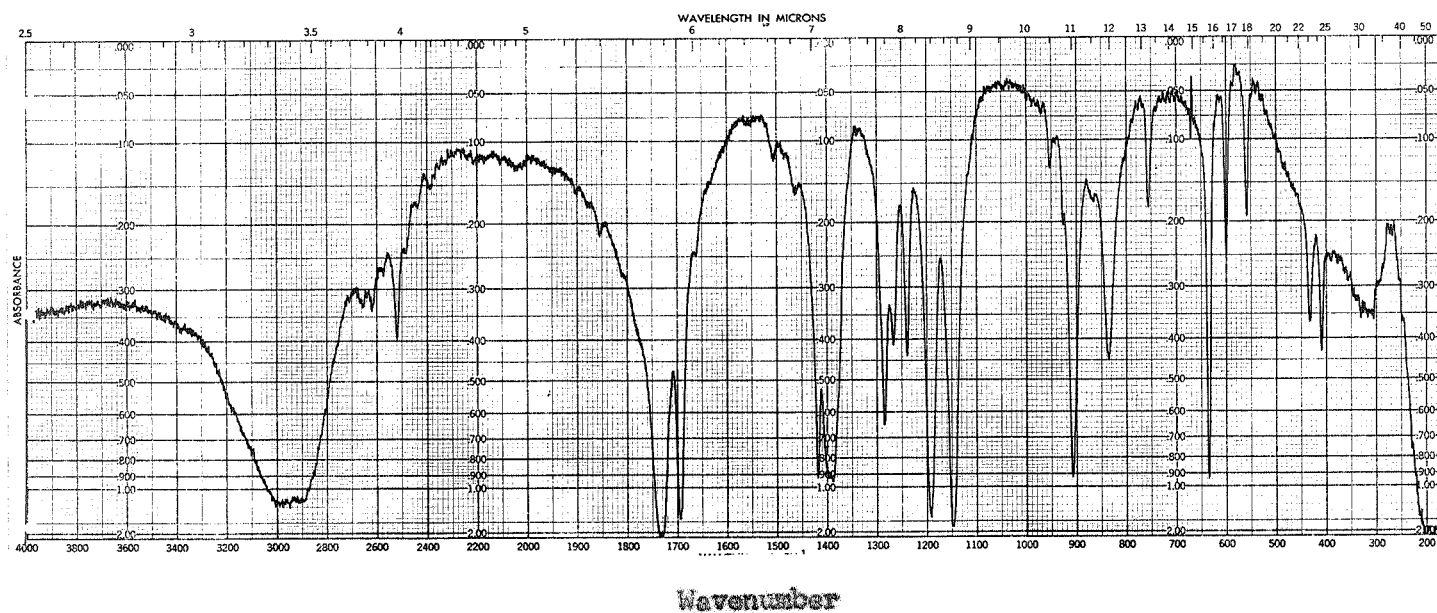


Figure II-16. Infrared Spectrum of a Pressed Pellet of Malonic Acid and CsCl Ground Together.

Table II-1 lists all of the salts studied in the present work and gives their behavior upon grinding, pressing, and heating (excepting CsCl and anhydrous NaBr) with malonic acid. Reaction I, the "normal" decarboxylation, seems to be the exception rather than the rule. Reaction II, the double decomposition or salt formation reaction, occurs to some extent in most of the salts studied in this work. Reaction II, excluding the dehydration steps, has been reported previously by Amakasu and Ito.³ The conclusion reached by these workers was that Reaction II proceeded only in those pellets containing a fairly high amount of moisture. This conclusion was not substantiated in the present work. When dried KBr was used, Reaction I predominated. However, when dried KCl was used, Reaction II predominated. When NaBr, dried in the same manner as the KCl just mentioned, was used, Reaction III occurred. Reaction I occurred both when KBr and malonic acid were ground in a dry box and when ground in the atmosphere. Further work is necessary to ascertain the conditions which control the behavior of malonic acid in the various alkali halide salts.

II-3: Experimental

II-3-1: Preparation of Alkali Halide-Malonic Acid Pressed Pellets

Table II-2 summarizes the source of the alkali halides used and the methods used in preparing the alkali halide pellets containing malonic acid.

Table II-1

Summary of Behavior of Malonic Acid In Various Alkali Halide Matrices

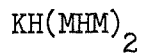
Alkali Halide	Behavior by Reaction Type (see II-1) and Comments
NaCl	Undergoes Reaction I. Good material for pellets. Difficult to render anhydrous. Some water evident in spectrum of pellets used.
NaBr	Undergoes Reactions I, II, or III, depending upon amount of water present.
NaI	Transmittance of pellets too low to obtain useable spectra.
KCl	Undergoes Reactions I and II. Good material for pellets.
KBr	Undergoes Reaction I. Good material for pellets.
KI	Undergoes Reaction II and some Reaction I. Good material for pellets.
RbCl	Undergoes Reactions I and II. Very good material for pellets.
RbBr	Undergoes Reaction I. Good material for pellets. Some water evident in spectrum of pellets used.
RbI	Undergoes Reaction I. Best of all materials used for pellets.
CsCl	Undergoes Reaction III. Independent of amount of water present.
CsBr	Undergoes Reaction I. Poor material, for pellets. No water evident in spectra of pellets used.
CsI	Undergoes Reactions I and II. Fair material for pellets. No water evident in spectra of pellets used.

Table II-2

Summary of Source of Alkali Halides Used and Method of Preparation
of Alkali Halide-Malonic Acid Pellets

Salt	Source*	Drying*	Preparation* Procedure
NaCl	Fisher	Yes	II
NaBr	Brinkman	No	I
NaBr	Brinkman	Yes	I
NaI	Brinkman	No	II
KCl	Fisher	Yes	I
KBr	Fisher, Harshaw, Brinkman	Yes	I
KI	Brinkman	Yes	I
RbCl	Brinkman	No	II
RbBr	Brinkman	Yes	I
RbI	Brinkman	No	II
CsCl	Brinkman	No	II
CsBr	Brinkman	No	II
CsI	Brinkman	No	II

*See Introduction and General Experimental Section.

II-3-2: Preparation of Potassium Hydrogen Di-monohydrogen Malonate

KH(MHM)_2 was prepared by two different procedures. The first of the methods of preparation involved weighing potassium hydroxide and malonic acid in a 1:2 mole ratio. The two preweighed portions were then dissolved in separate flasks of distilled water with addition of enough ice to make the mixtures slushy. These two slushy mixtures were then mixed together slowly. In order to prevent the heat of reaction from decomposing the reaction product, the reaction flask was also kept cool by means of an ice water bath. The mixture was then allowed to warm to room temperature and most of the water was removed using a rotary evaporator and a water aspirator. The remaining water was removed by reduced pressure using a vacuum pump.

In order to prepare KH(MHM)_2 by another method it is necessary only to dissolve malonic acid in acetone or diethyl ether and then add solid KOH which was prewashed with distilled water. The KH(MHM)_2 forms directly on the surface of the pellets as an insoluble material. After removal of the excess solid KOH, the solvent is evaporated from the product. The product is then washed with diethyl ether and the excess ether is evaporated. This quick and easy method of preparing KH(MHM)_2 gives reliable results as evidenced by the consistency in appearance of the infrared spectrum of the reaction product in each case. The elemental analysis* of the product is given below along with the calculated percentage

*All elemental analyses were done by Galbraith Laboratories, Inc., P. O. Box 4187, 2323 Sycamore Drive, Knoxville, Tennessee. 37921.

for $\text{KHC}_6\text{H}_7\text{O}_8 \cdot \text{KH}(\text{MHM})_2$.

Found (%) C, 29.87; H, 3.08, K, 13.88; O (obtained by difference),
53.17.

Theoretical (%) C, 29.68; H, 2.85; K, 15.85; O, 51.62,

The discrepancy in the values can possibly be attributed to approximately 0.4 moles of excess malonic acid per mole of $\text{KH}(\text{MHM})_2$.

II-3-3: Preparation of a Product With a KOH-Malonic Acid Mole Ratio of 1:1.5.

The method of preparation of this material is the same as the first method of preparation described above for $\text{KH}(\text{MHM})_2$ except that the KOH:Malonic acid mole ratio is in this case 1:1.5. The infrared spectrum (Fig. II-10) was nearly identical to that of $\text{KH}(\text{MHM})_2$, (Fig. II-9), the only difference being the appearance of a band at 3300 K which might be ascribed to the excess KOH.

II-3-4: Preparation of Potassium Hydrogen Malonate $\text{K}(\text{MHM})$

The method of preparation of this compound is the same as the first method of preparation described above for $\text{KH}(\text{MHM})_2$. In this case the KOH-malonic acid mole ratio was 1:1. The elemental analysis of the product, $\text{KHC}_3\text{H}_2\text{O}_4$ after two recrystallizations from distilled water is given below:

Found (%): C, 23.58; H, 3.29; K, 26.57; (O obtained by difference),
46.56.

Theoretical (%): C, 25.35; H, 2.11; K, 27.57; O, 44.97.

The discrepancies in the analysis can possibly be attributed to residual water in the product.

Another method of preparation of $K(MHM)_2$ involves heating $KH(MHM)_2$ under reduced pressure. Application of gentle heat to a partially evacuated flask containing $KH(MHM)_2$ results in the sublimation of malonic acid leaving a residue of $K(MHM)_2$, as evidenced by the infrared spectrum of the product.

II-3-5: Preparation of a Material with A KOH-Malonic Acid Mole Ratio of 1.5:1

The method of preparation of this material is the same as the first method described above for preparation of $KH(MHM)_2$ except that the KOH-malonic acid mole ratio used was 1.5:1. The infrared spectrum (Fig. II-12) of the product obtained indicated that the product might be a mixture of $K(MHM)_2$ and $K_2M \cdot H_2O$ (Figs. II-11 and II-13).

II-3-6: Preparation of the Dipotassium Malonate-Monohydrate $K_2(C_3H_2O_4) \cdot H_2O$ or $K_2M \cdot H_2O$

$K_2M \cdot H_2O$ is prepared by the same method as that described first above for $KH(MHM)_2$. In this case the KOH-malonic acid mole ratio used was 2:1.

The elemental analysis is given below along with the calculated values for $K_2C_3H_2O_4 \cdot H_2O$.

Found (%): C, 18.17; H, 1.52; K, 39.59; O (obtained by difference), 50.72.

Theoretical (%): C, 18.15; H, 2.02; K, 39.42.

The discrepancies between the found and theoretical values can possibly be explained by incomplete formation of the hydrate.

II-3-7: Preparation of Anhydrous Dipotassium Malonate $K_2C_3H_2O_4$, or $K_2(M)$

This product was prepared by a thermal dehydration of $K_2M \cdot H_2O$ under reduced pressure. The $K_2M \cdot H_2O$ was placed under a reduced pressure of approximately 0.5 torr and heated to approximately 200° . This procedure resulted in a loss of water from $K_2M \cdot H_2O$ forming K_2M . This fact was confirmed by the infrared spectrum (Fig. II-12) and by recrystallization of K_2M from water, reforming $K_2M \cdot H_2O$ as evidenced by the infrared spectrum (Fig. II-13).

Test for the Presence of HCl from the KCl-Malonic Acid Reaction

II-3-8 Mixtures

An attempt was made to observe HCl evolution from several heated KCl-malonic acid pellets of the composition used in the research. Several pellets were placed in a 10 cm gas cell fitted with NaCl windows, and the cell placed in an oven at 100° . The gas cell was then removed intermittently, placed in the infrared spectrometer and the spectrum recorded. Upon conclusion of the total heating interval of 48 hours, some of the pellets were removed from the gas cell, placed in an infrared spectrometer and the spectrum recorded. The infrared spectrum showed evidence of the occurrence of the double decomposition reaction, but no HCl was detected in the gases above the pellets in the gas cell.

A loose power mixture of pre-dried KCl and malonic acid (approx. 10% malonic acid by weight) was placed in a 10 cm gas cell fitted with NaCl windows. The cell was then kept at approximately 100° for several days. Intermittently, the cell was removed from the oven, placed in the infrared spectrometer, and the spectrum of the gases over the loose powder obtained. In order to determine whether the above decomposition (salt formation) reaction was proceeding under the conditions maintained above, another portion of the same starting material was placed in a gas cell and heated under the same conditions. At certain intervals, portions of the mixture were removed, pressed into a pellet, placed in the infrared spectrometer and the spectrum obtained. These spectra demonstrated that the double decomposition reaction was indeed occurring under these conditions.

Neither of the experiments outlined above enabled the observance of evolved HCl from either the pellets or the loose powder mixture nor did the pellets obtained from the experiments show any evidence of trapped HCl.

In an effort to determine whether HCl could be observed in any case under the experimental conditions of the experiments outlined above, the following experiment was devised. Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), which was shown to give off HCl when heated, was mixed with KCl, pressed into a pellet and the pellet heated at 120° . The infrared spectrum of the pellet gave evidence of the decomposition of the $\text{NH}_2\text{OH}\cdot\text{HCl}$, but no indication of HCl trapped in the matrix. Several pellets of $\text{KCl-NH}_2\text{OH}\cdot\text{HCl}$ were then prepared, sealed in a gas cell, and

heated at 120° C. The infrared spectrum of the gases above the pellets in the cell, obtained intermittently during heating, showed that HCl had been evolved from the $\text{KCl-NH}_2\text{OH}\cdot\text{HCl}$ pellets.

II-3-9: Preparation of Anhydrous NaBr Pellets

The method used to dry the NaBr is the same as that described in the General Introduction and Experimental Section under Pellet Preparation. The dried NaBr was mixed with predried malonic acid by means of an agate mortar in a glove box which was purged with dry air. A pellet die was also placed in the glove box, and, at various grinding intervals, filled with the desired amount of the mixture and removed for pressing of the pellets.

II-3-10: Preparation of CsCl Pellets

The pellets of CsCl and malonic acid were prepared by grinding predried CsCl, or CsCl used as received, and malonic acid in the laboratory atmosphere in an agate mortar and then pressing the material into a pellet. The pellets of moistened CsCl and malonic acid were prepared in the same manner with the exception that various amounts of distilled water were added to the CsCl before grinding.

II-3-11: NMR Spectra of Malonic Acid

The nmr spectra of malonic acid with acetone as a solvent was obtained from a Varian HA-60 High Resolution NMR Spectrometer. In an attempt to obtain the nmr spectrum of the product of the anomalous behavior of malonic acid in CsCl, acetone was added to a CsCl-malonic

acid mixture which had been ground in an agate mortar. The nmr spectrum of the resultant solution matched that of malonic acid. The infrared spectrum of the pellet pressed from the CsCl-malonic acid mixture which had been ground, washed with acetone and the acetone evaporated showed no absorption bands indicating that the malonic acid was completely removed from the CsCl.

Thin-layer Chromatography

Malonic acid and CsCl (approximately 5% malonic acid by weight) were ground together in an agate mortar. To this mixture, approximately 5 mls of acetone were added and the mixture stirred for approximately one minute. Two to three microliters of this solution along with a reference spot (2 microliters of an acetone solution of malonic acid which was approximately 5% malonic acid by weight) were placed at the bottom of a Thin-layer Chromatographic plate covered with silica gel. The plate was developed with n-hexane.

The above procedure was then repeated using acetone as the solvent and a 50% n-hexane:50% acetone solution as developer.

The entire procedure described above was then repeated using ethyl ether as a solvent for both the CsCl-malonic acid mixture and the reference solution. The developing solutions were the same as those described above.

PART II

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PART III

The Kinetics of Thermal Decarboxylation of Malonic Acid in
KBr and in RbBr.III-1: Introduction and Literature Survey

The years following a report¹ of research into the thermal decomposition of aqueous solutions of malonic acid have brought a number of papers dealing with the thermal decarboxylation of malonic acid and its derivatives. Hinshelwood² and Laskin³ studied the decarboxylation of molten malonic acid and found the reaction to be first order in appearance of CO₂. Many workers⁴⁻¹³ have investigated the thermal decarboxylation of C¹³ enriched malonic acid in various solvents. Others¹⁴ have investigated the thermal decarboxylation of malonic acid-d₄ in the molten state. Investigations of the decarboxylation reaction have been carried out in numerous solvents by Clark¹⁵⁻¹⁶ and by others²⁷⁻³².

The large volume of research on the thermal decarboxylation of malonic acid has generated a number of proposed mechanisms for the reaction. Fairclough²⁹ proposed a mechanism for the decarboxylation of α -unsaturated acids in general which involved the formation of a cyclic intramolecularly hydrogen bonded intermediate. Partial substantiation of this mechanism comes from research, reported by Kenyon and Ross,³⁰ showing evidence of the formation of a carbon-carbon double bond during decarboxylation. However, the fact that the decarboxylation of molten malonic acid exhibits no deuterium isotope effect¹⁴ shows that the formation or dissociation of this cyclic

intermediate is not the rate determining step. Frankel et al.³¹ have proposed a bimolecular reaction mechanism in which the rate determining step is the formation of a complex between the electrophilic carboxyl carbon atom and the nucleophilic solvent molecules. Frankel's mechanism is consistent with the observed data for the thermal decarboxylation of malonic acid and also for α -unsaturated acids in general.

In the work reported here, the thermal decarboxylation of malonic acid has been studied in various alkali halide matrices. In most of the salts studied, useful data could not be obtained due to a competition reaction involving malonic acid and the alkali halide studied. However, in some of the salts studied (e.g., KBr, and RbBr) the double decomposition reaction proceeded only to a negligible extent, allowing the collection of data which could be used to determine reaction rate constants. The decarboxylation of malonic acid in alkali halide matrices is shown to be first order in disappearance of malonic acid.

Other workers³³⁻³⁷ have studied effects upon the kinetics of other reactions when the reactants are suspended in salt matrices. The net results of the research done by these workers show an overall effect upon the energy of activation of a reaction when the reactants are suspended in salt matrices. There is, however, no evidence of variation of activation energy from salt to salt.

III-2: EXPERIMENTAL

Constant Temperature Bath

The constant temperature bath consisted of a Fisher Unitized Bath filled with either Fisher Bath Wax (flash point 325°) or Ucon oil 50-HB-280-X (obtained from Union Carbide Chemicals Corporation, Charleston, West Virginia). The Ucon oil, stabilized with phenothiazine enabled routine prolonged operation of the bath at temperatures up to 170° . Operating temperatures higher than 170° could be maintained for shorter periods of time. The Fisher bath wax could not be maintained at temperatures greater than 150° , due to decomposition of the wax. The fact that the Ucon fluid is water soluble enables convenient and easy cleaning of equipment.

The temperature of the bath was maintained by a mercury expansion controlled electronic relay system. In the bath, two heating coils were placed, one of which was controlled by the electronic relaying system, the other by an auto-transformer. This system enabled temperature control within a ± 0.05 degrees temperature range. A Philadelphia thermometer was used during bath operation to obtain the range of temperature variation. The actual temperature of the bath was obtained by a standardized thermometer. The thermometer was standardized against National Bureau of Standards thermometer set number 51364, and the temperature measured during an experimental run was corrected accordingly.

A plywood rack was constructed for the bath in order to enable the placement of the reaction tubes in the bath. The reaction tubes

used were standard 6-inch test tubes stoppered with corks.

Procedure Used to Obtain Kinetic Data

The procedure used in the preparation of alkali halide pellet mixtures has been described previously. In preparation for a kinetic run using the multipellet method, 10 to 15 pellets were pressed, weighed to the nearest 0.01 milligram and the infrared spectrum of each obtained. The absorbances of the initial spectra were then used to establish the zero time absorbances of each pellet. The pellets were placed individually in test tubes and the tubes placed in the constant temperature bath. Each pellet was then removed from the bath upon elapse of a specific amount of time. The times were obtained by means of a stopwatch which was allowed to run continuously throughout a kinetic run. Upon completion of the pellet heating times, the spectrum of each pellet was obtained after the pellet was repressed. The repressing was necessitated by the fact that, upon heating, the pellets became opaque and expanded slightly, as evidenced by the inability to replace the pellets into the pellet die. The repressing procedure resulted in a slight weight loss which necessitated correction of the absorbances obtained after repressing. Most of the weight loss during repressing was the result of the necessity to sand the edges of the pellets in order to replace them in the pellet die.

After obtaining the spectra of all of the heated pellets the band transmittances, or absorbances, were then obtained by the baseline technique. These values were punched on computer data cards and the data

analyzed by a computer program written specifically for this work. The program is listed in the Appendix.

III-3: Results and Discussion

Absorbance vs. Pellet Weight Plots

Figure III-1 shows a plot of absorbance versus pellet weight for the infrared absorption bands at 3000 K in malonic acid. The corresponding data for the other bands are comparable. The fact that, within experimental errors, the calculated intercept of the line is at the origin, means that the absorbances of each pellet can be corrected to a standard pellet weight by way of a simple weight ratio. In this work, the standard pellet weight (W_o) was chosen as 0.20000g. The infrared band absorbance of a pellet of weight W_t can then be corrected to the absorbance of a pellet of weight W_o by the following formula:

$$A_{\text{corr}} = A_t (W_o/W_t)$$

or in this case

$$A_{\text{corr}} = A_t (0.20000/W_t)$$

A_t is the experimentally measured absorbance and W_t the experimentally determined weight of the pellet. A_{corr} is then the absorbance which a pellet, of weight W_t , would have exhibited if it had weighed 0.2000 g.

These corrected absorbances lend themselves quite well to calculations of the variance of the absorbance measurements. The calculated variances give an indication of the errors associated with the measurement of the absorbances, as well as the absorbance measurement errors

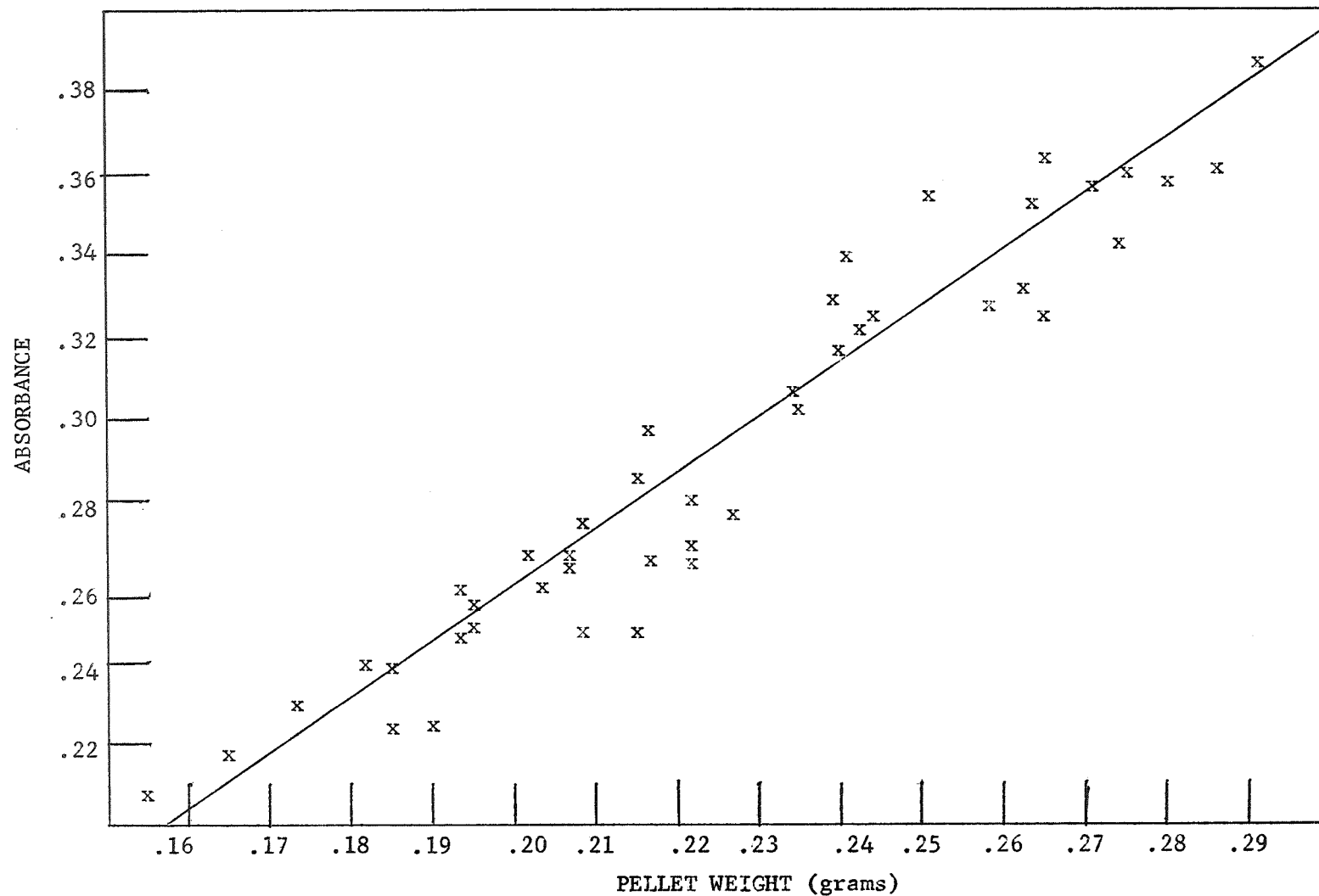


Figure III-1. Plot of Initial Absorbance versus Pellet Weight for the 3000 K Infrared Absorption Band in the Infrared Spectrum of Malonic Acid in KBr,

associated with the inhomogeneity of the pellet mixture. The variances of the initial absorbances of each of the bands plotted is given in Table III-1. These absorbances were obtained from approximately 50 pellets all of which were pressed from the same pellet mixture.

Table III-1

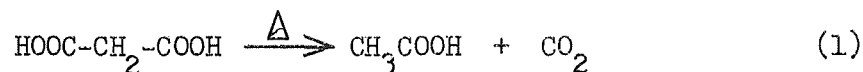
Variances ($\times 10^3$) of absorption of 9 of the major bands of malonic acid as average variances obtained from 5 kinetic runs made on the same bulk pellet mixture

Absorp- tion Band(K)	3000	1700	1440	1310	1220	1175	900	760	650
Variance	.42	2.27	.62	.56	1.13	1.01	.82	.50	.53

Reaction Order Plots

Previous work³³⁻³⁷ has shown that in KBr pellets, the absorbance of the sample varies linearly with concentration over the ranges of concentrations used in this work. By making pellets of mixtures of KBr and malonic acid in varying concentrations and obtaining their infrared spectrum, it was shown that all 9 of the major absorption bands of malonic acid obey Beer's Law over the concentration range of interest in this work.

The thermal decarboxylation of malonic acid can be written



Since absorbance is directly proportional to concentration the rate law of the reaction can be written as

$$-\frac{d[A]}{dt} = k [A]^n \quad (2)$$

Taking the logarithm of both sides of equation (2)

$$\log \left[-\frac{d[A]}{dt} \right] = \log k + n \left[\log [A] \right] \quad (3)$$

Plotting $\log (\Delta A / \Delta T)$ versus $\log (A)$ should give a straight line of slope n , the reaction order of the component whose absorbance is used.

The quantity $(\Delta A / \Delta T)$ can be determined by either of two methods (1) by plotting A versus t and obtaining the slope of the resulting curve at various A values, or (2) by calculating $(\Delta A / \Delta T)$ using the actual data. The latter method means choosing values of absorbance at various times and calculating the change in absorbance (ΔA) during the time interval (Δt) . The ratio $(\Delta A / \Delta t)$ is then plotted against the logarithm of the starting absorbance chosen. The second method described was used to obtain Figures III-2 through III-4.

Plots of the equation for the absorbance of the 3000 K band are shown in Figures III-2 through III-4 for the decarboxylation malonic acid at three different temperatures.

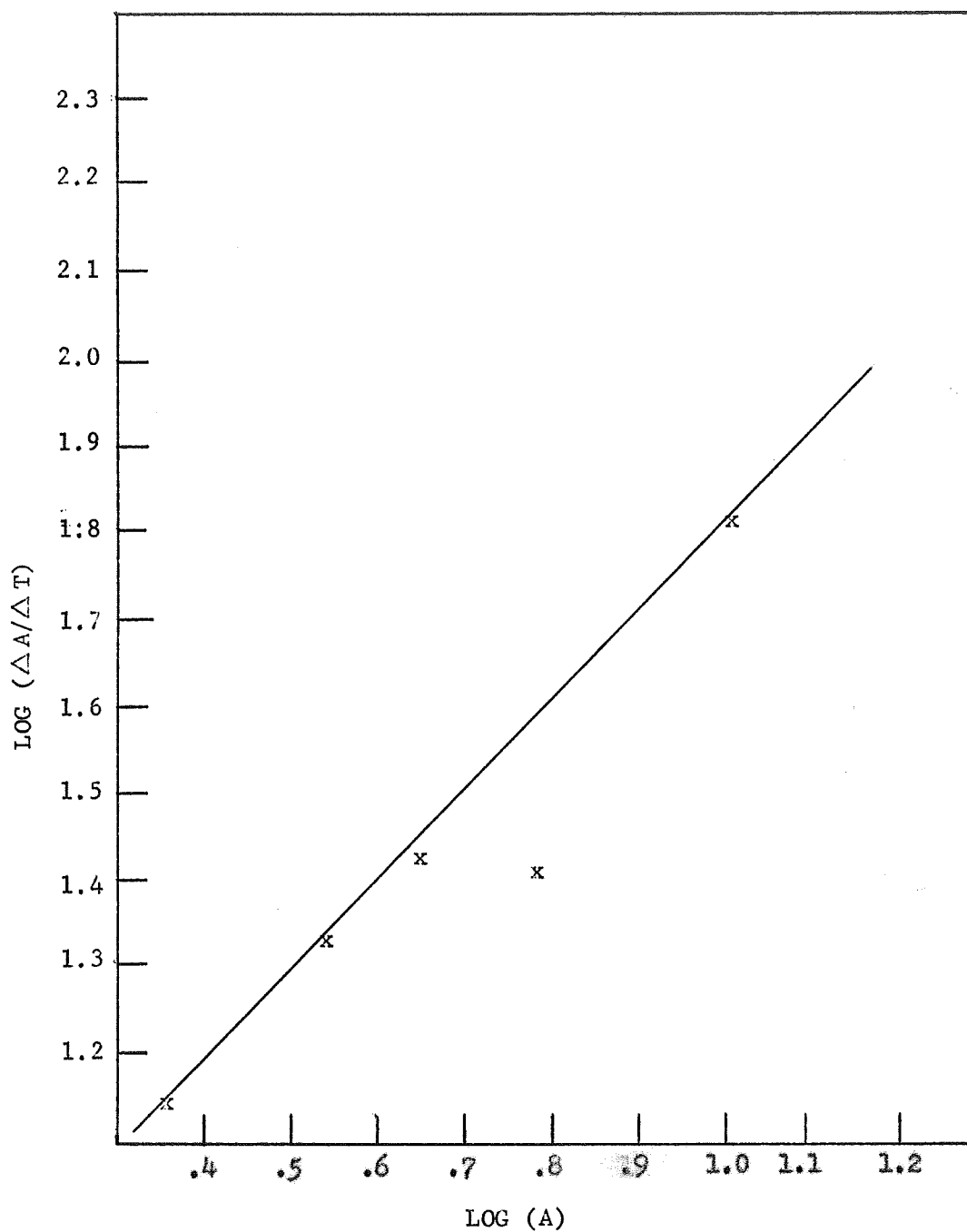


Figure III-2. Thermal Decarboxylation Reaction Order Plot for the 3000 K Infrared Absorption Band of Malonic Acid at 144.9° in KBr.

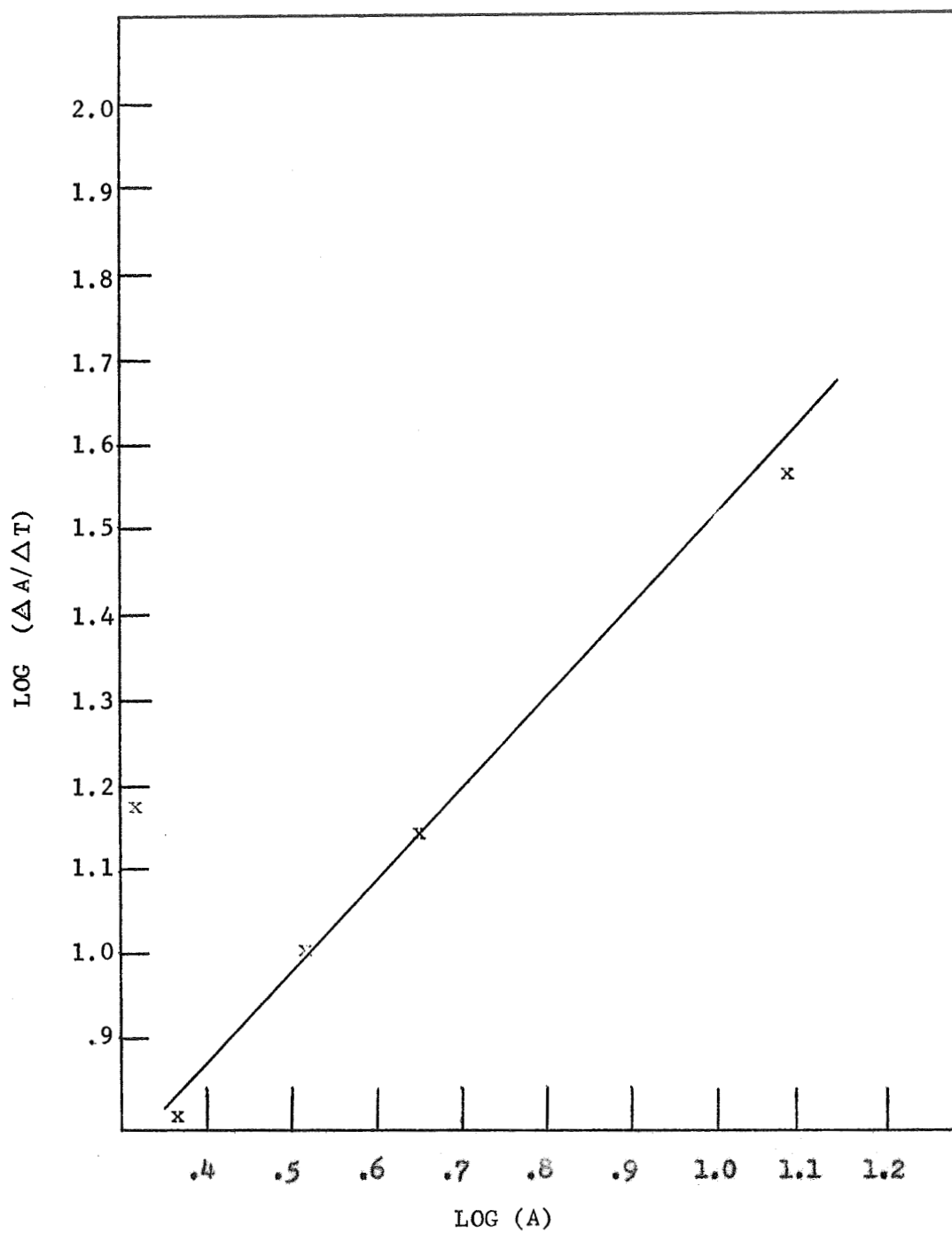


Figure III-3. The Thermal Decarboxylation Reaction Order Plot for the 3000 K Infrared Absorption Band of Malonic Acid at 161.0° in KBr.

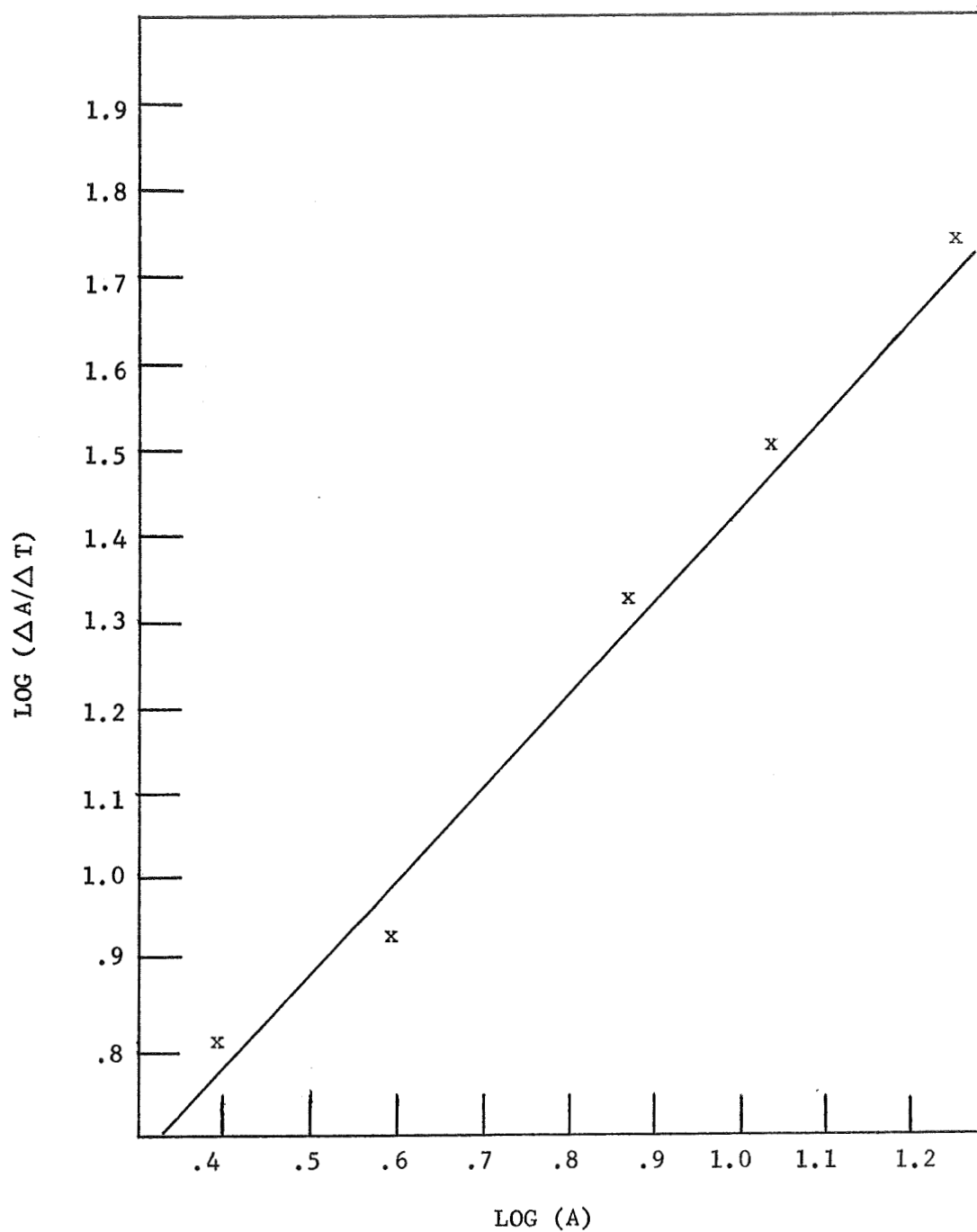


Figure III-4. The Thermal Decarboxylation Reaction Order Plot for the 3000 K Infrared Absorption Band of Malonic Acid at 167.0° in KBr.

The slopes of the resulting plots (Figures III-2 through III-4) are 1.18 at 144.9°, 1.15 at 161.0° and 1.08 at 167.0°. The fact that these values of the slopes are close to 1 enables the assumption that the thermal decarboxylation of malonic acid in alkali halide matrices is a first order, or pseudo-first order, reaction.

Rate Constant Plots and Data

For first order reactions, the integrated rate expression is

$$kt = \ln \frac{C_o}{C_t} \quad (4)$$

where C is the initial concentration and C_t is the amount of reactant remaining at time t.

From Beer's Law

$$A = abc \quad (5)$$

where b is the thickness of the pellet in mm, C is the concentration of the sample in the pellet in moles/ml and a is the absorptivity of a particular absorption band. In the case of a circular pellet

$$V = \pi r^2 b = W_t / d \quad (6)$$

where r is the radius of the pellet, d is the density of the pellet and W_t is the weight of the pellet at time t. Rearranging equation (6) and substituting into equation (5) gives

$$C_t = \frac{\pi A_t r^2 d}{a W_t} \quad (7)$$

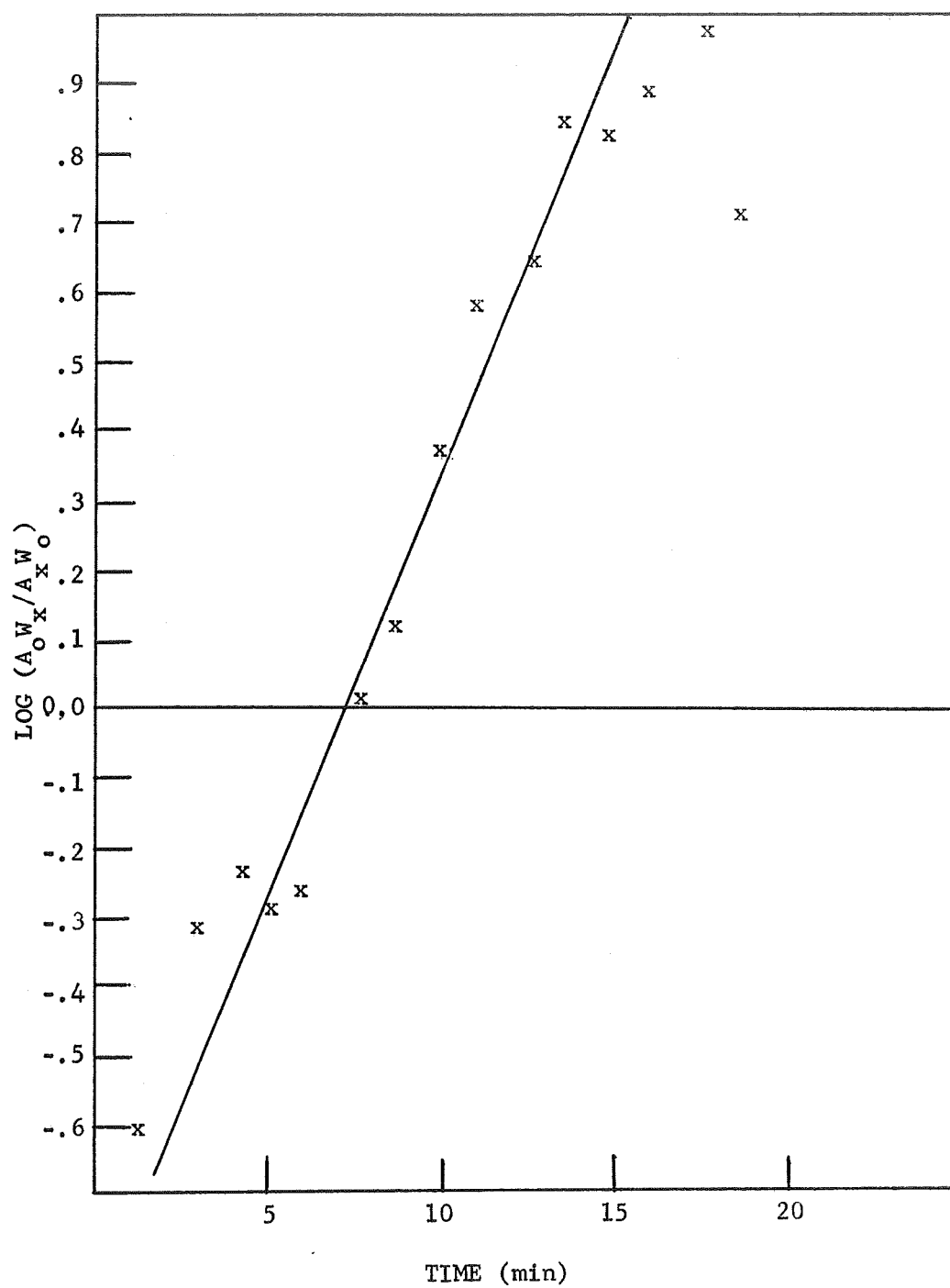


Figure III-5. Rate Constant (k') Plot of the 3000 K Band for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1°C.

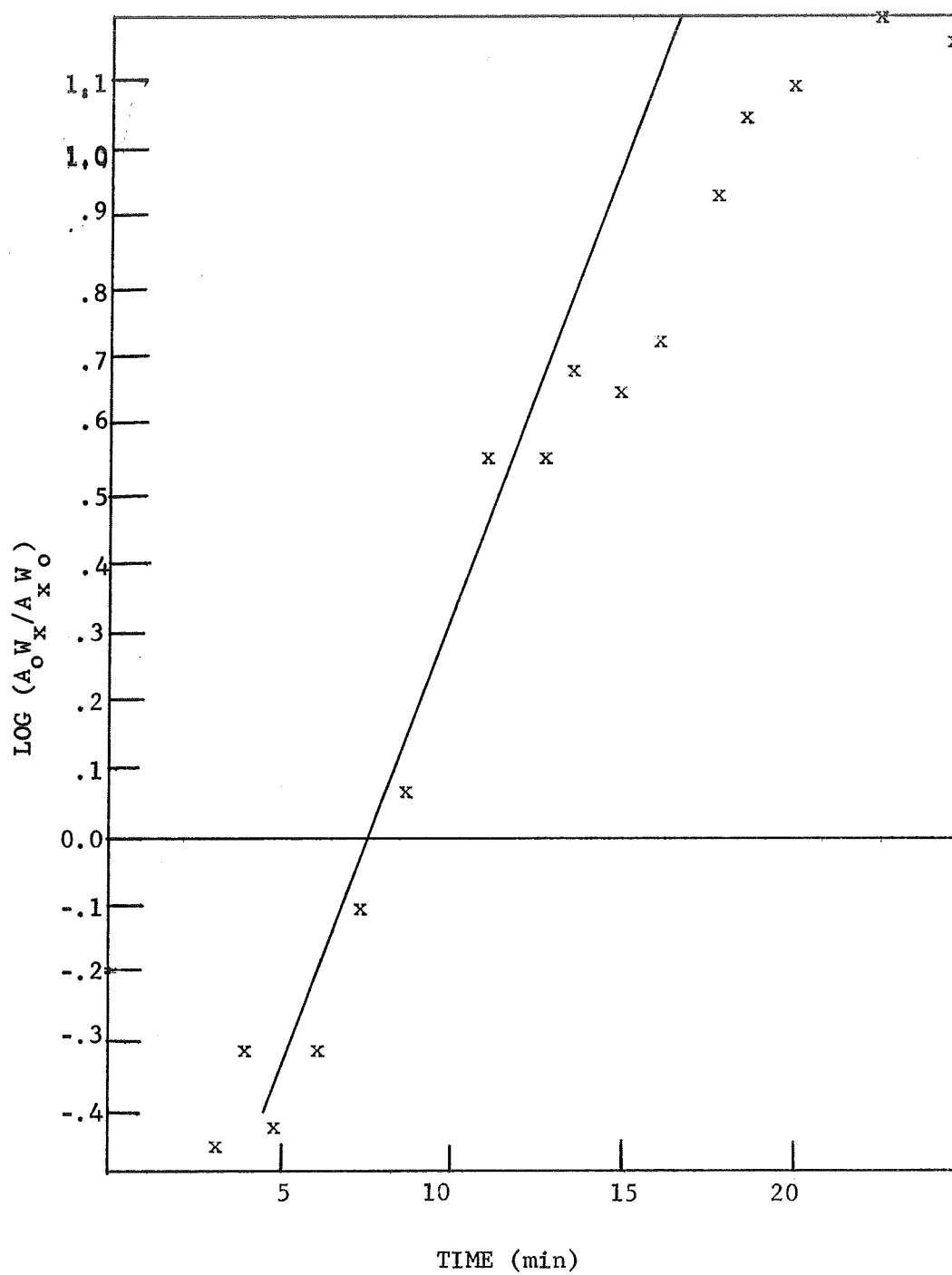


Figure III-6. Rate Constant (k') Plot of the 1700 K Band for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1° .

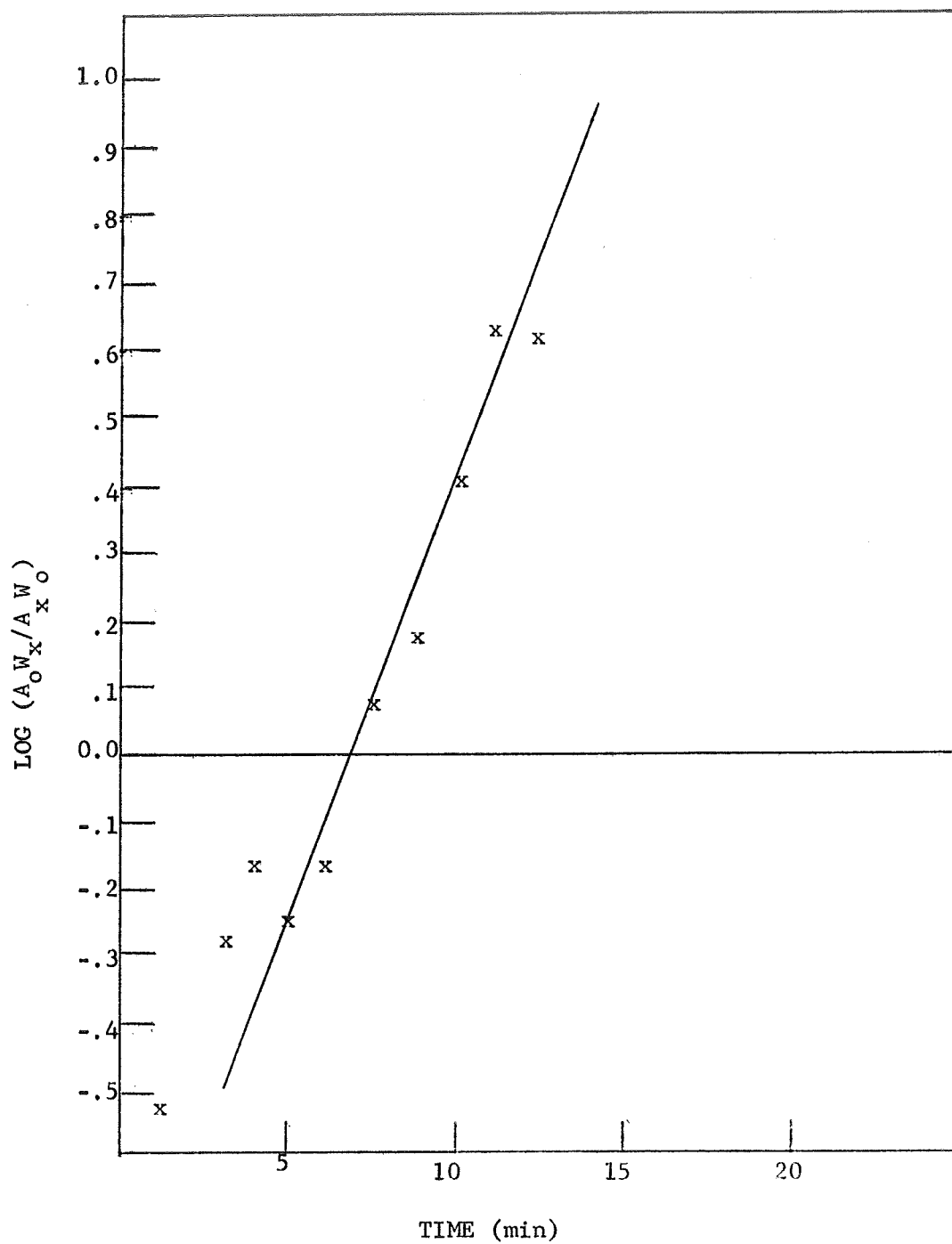


Figure III-7. Rate Constant (k') Plot of the 1440 K Band for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1°C.

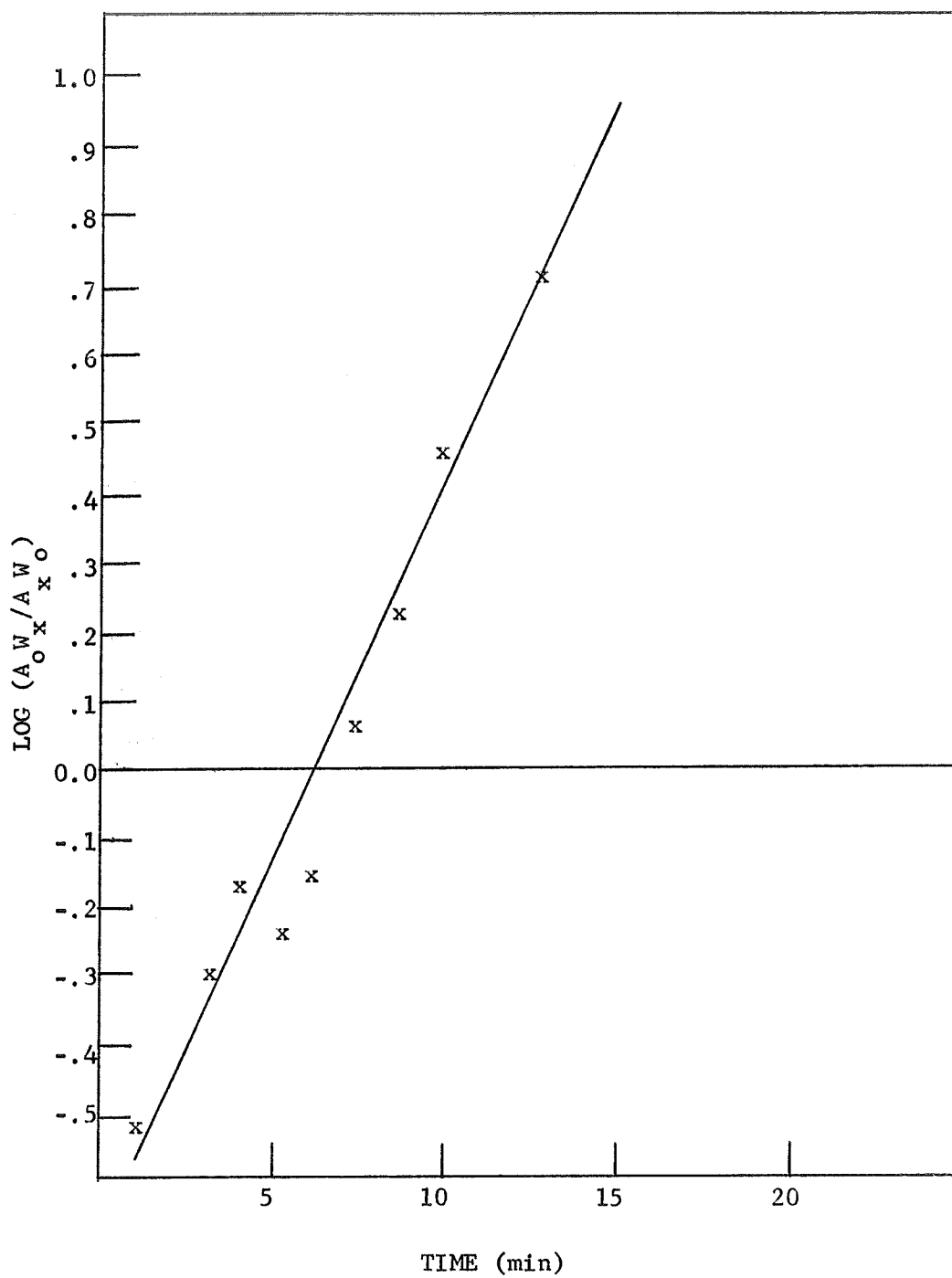


Figure III-8. Rate Constant (k') Plot of the 1220 K Band for Thermal Decarboxylation of Malonic Acid in KBr at 158.1°C.

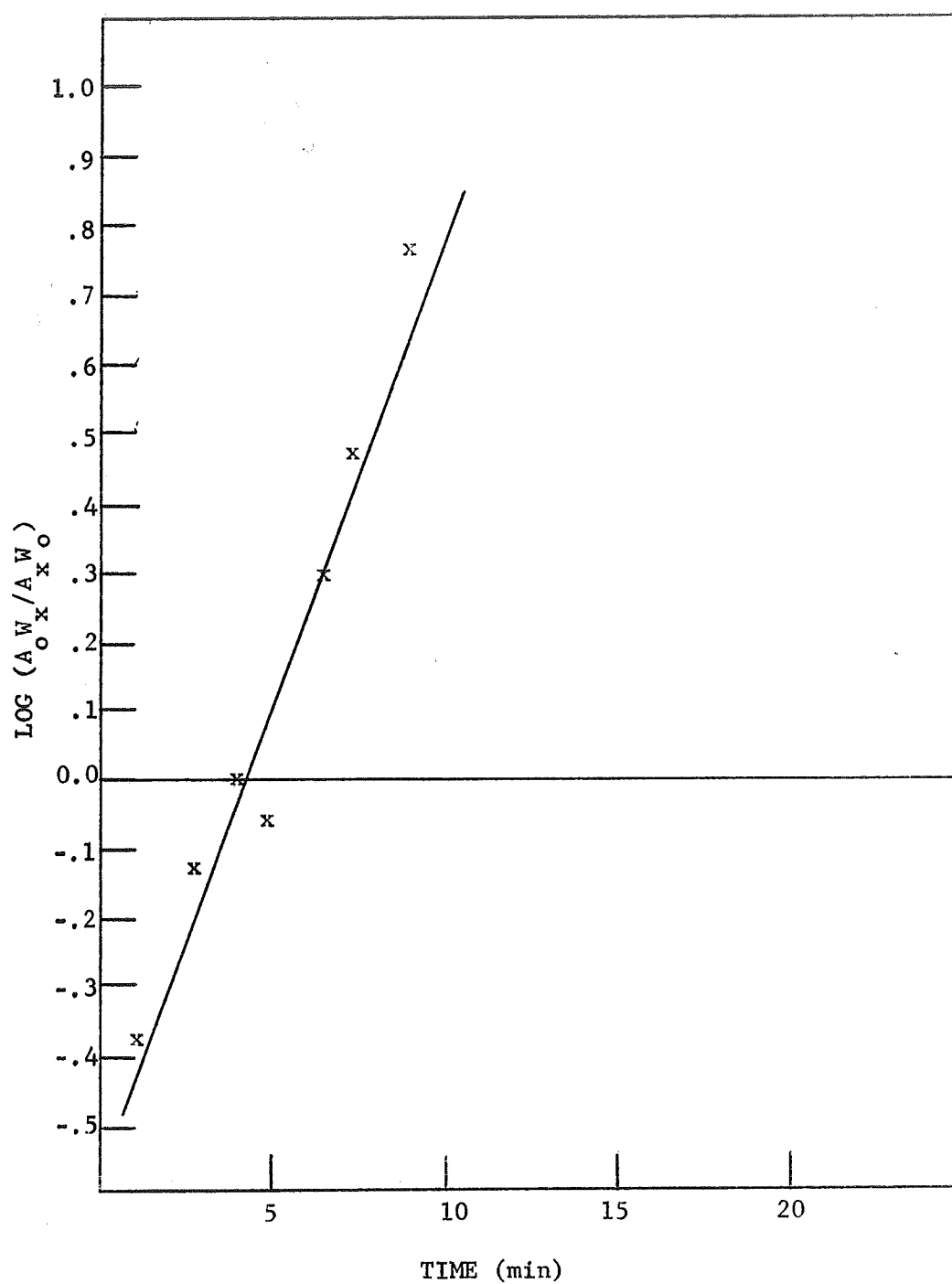


Figure III-9. Rate Constant (k') of the 900 K Band for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1° .

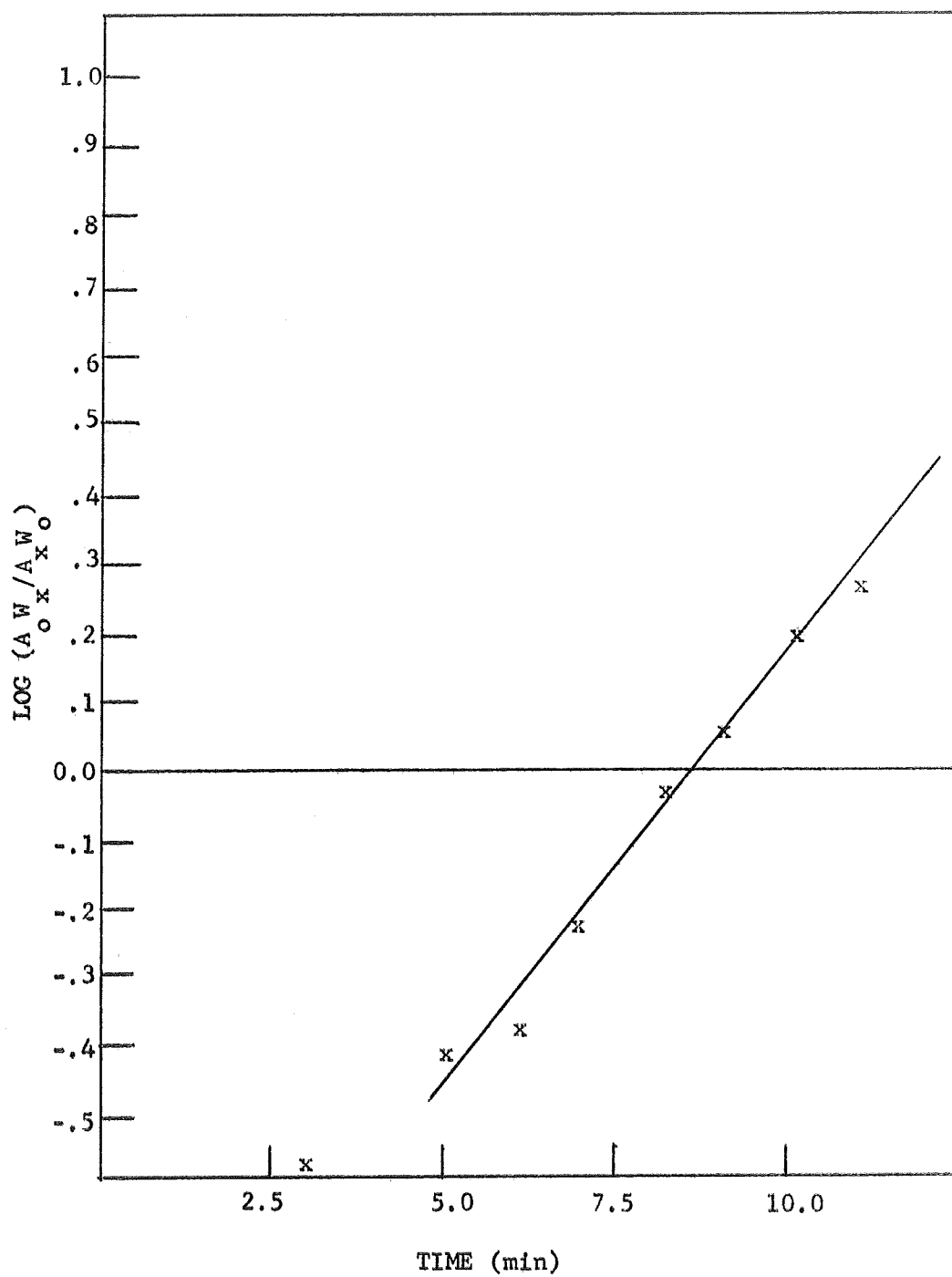


Figure III-10. Rate Constant (k') Plot of the 3000 K Band for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5°.

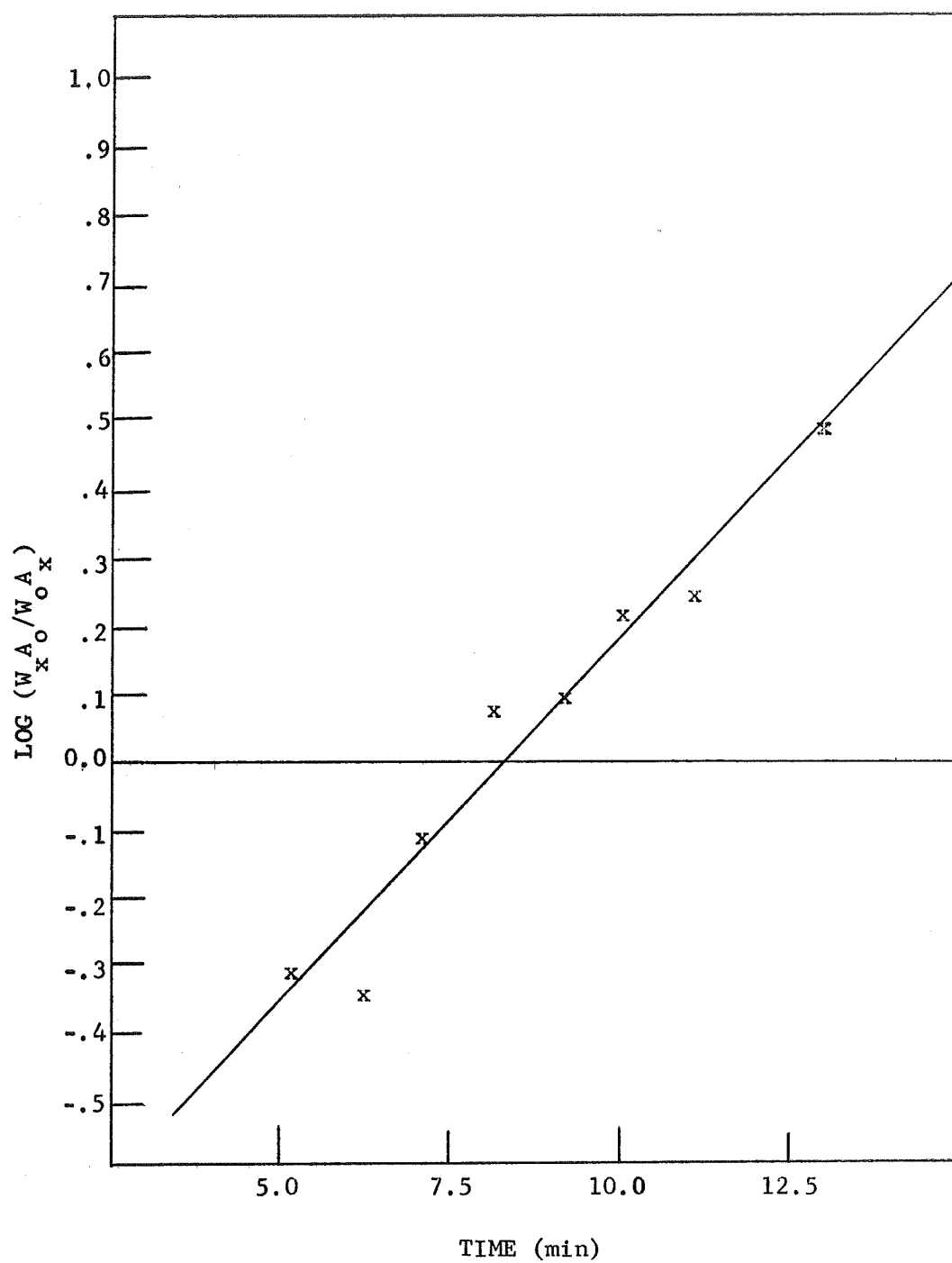


Figure III-11. Rate Constant (k') Plot of the 1700 K Band for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5° .

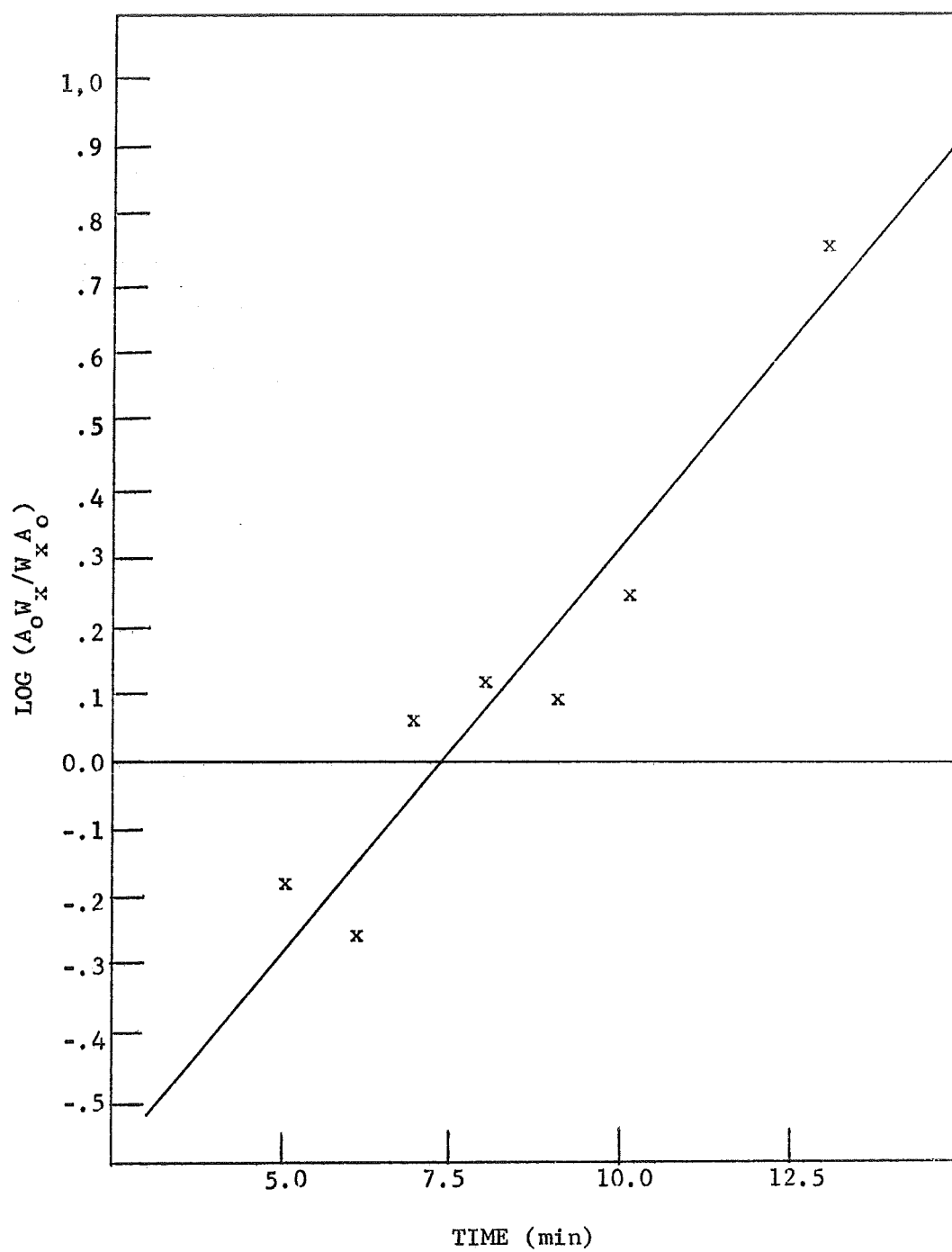


Figure III-12. Rate Constant (k') of the Plot of the 1440 K Band for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5° .

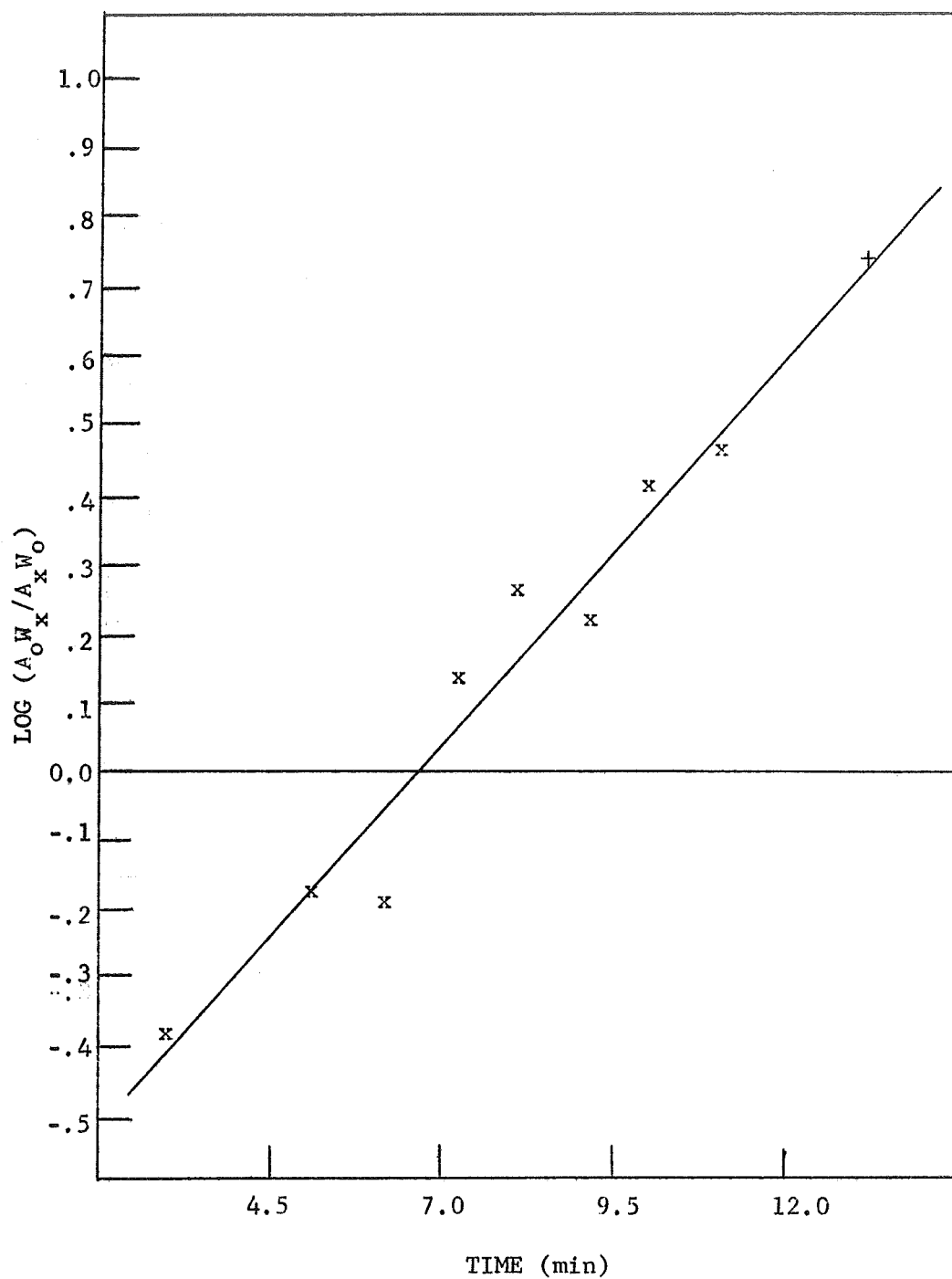


Figure III-13. Rate Constant (k') Plot of the 1220 K Band for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5°C.

Table III-3. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 142.0°.

[illegible]

Table III-4. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 153.2° .

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.773	1.648	0.884	0.735	1.286	1.079	0.771	0.233	0.680		0.27748
2	0.786	2.045	0.988	1.175	1.449	1.176	0.798	0.242	0.716		0.27060
3	0.370	0.693	0.462	0.378	0.597	0.471	0.414	0.148	0.291		0.18185
4	0.597	1.596	0.703	0.543	0.983	0.770	0.679	0.167	0.677		0.20078
5	0.711	1.176	0.619	0.504	0.887	0.653	0.530	0.147	0.509		0.19614
6	0.606	1.673	0.726	0.558	1.148	0.820	0.591	1.184	0.507		0.20344
7	0.547	1.320	0.621	0.490	0.921	0.686	0.524	0.154	0.539		0.19757
8	0.525	1.308	0.604	0.481	0.906	0.673	0.527	0.142	0.509		0.18866
9	0.551	1.334	0.638	0.528	0.943	0.692	0.562	0.186	0.560		0.19193
10	0.596	1.542	0.723	0.586	1.148	0.831	0.632	0.245	0.577		0.20860
11	0.604	1.571	0.682	0.578	1.122	0.843	0.625	0.191	0.622		0.20610
12	0.525	1.382	0.608	0.488	0.910	0.655	0.527	0.152	0.521		0.18953
13	0.470	1.036	0.530	0.420	0.799	0.579	0.452	0.129	0.463		0.16716
14	0.428	0.906	0.447	0.350	0.646	0.491	0.366	0.103	0.390		0.13215
15	0.427	0.935	0.479	0.387	0.704	0.539	0.422	0.123	0.436		0.14578
16	0.356	0.790	0.408	0.333	0.585	0.457	0.349	0.098	0.333		0.12315

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.00000
2	0.942	0.000	1.213	0.000	1.423	0.772	0.573	0.000	0.000	5.0	0.26390
3	0.225	0.555	0.246	0.000	0.274	0.242	0.090	0.000	0.000	10.0	0.18090
4	0.218	0.545	0.265	0.000	0.281	0.251	0.091	0.000	0.000	12.5	0.20033
5	0.095	0.241	0.128	0.000	0.131	0.176	0.033	0.000	0.000	15.0	0.19337
6	0.069	0.218	0.000	0.000	0.128	0.141	0.020	0.000	0.000	17.5	0.20003
7	0.053	0.158	0.000	0.000	0.092	0.114	0.000	0.000	0.000	20.0	0.19391
8	0.049	0.116	0.000	0.000	0.078	0.077	0.000	0.000	0.000	23.0	0.18614
9	0.040	0.106	0.000	0.000	0.068	0.072	0.000	0.000	0.000	25.0	0.19035
10	0.028	0.076	0.000	0.000	0.073	0.079	0.000	0.000	0.000	27.5	0.20505
11	0.022	0.072	0.000	0.000	0.060	0.078	0.000	0.000	0.000	30.0	0.20600
12	0.018	0.060	0.000	0.000	0.063	0.067	0.000	0.000	0.000	33.0	0.18847
13	0.023	0.046	0.000	0.000	0.053	0.055	0.000	0.000	0.000	35.0	0.16640
14	0.040	0.029	0.000	0.000	0.063	0.069	0.000	0.000	0.000	40.0	0.13072
15	0.046	0.036	0.000	0.000	0.049	0.048	0.000	0.000	0.000	45.0	0.14320

Table III-5. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 153.2°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
-0.089	0.000	-0.100	0.000	-0.003	0.172	0.133	0.000	0.000	5.0
0.213	0.094	0.272	0.000	0.336	0.286	0.660	0.000	0.000	10.0
0.437	0.466	0.423	0.000	0.543	0.485	0.872	0.000	0.000	12.5
0.866	0.681	0.677	0.000	0.824	0.563	1.198	0.000	0.000	15.0
0.934	0.879	0.000	0.000	0.944	0.759	1.473	0.000	0.000	17.5
1.008	0.914	0.000	0.000	0.991	0.773	0.000	0.000	0.000	20.0
1.028	1.045	0.000	0.000	1.060	0.937	0.000	0.000	0.000	23.0
1.140	1.097	0.000	0.000	1.137	0.982	0.000	0.000	0.000	25.0
1.313	1.298	0.000	0.000	1.187	1.013	0.000	0.000	0.000	27.5
1.434	1.340	0.000	0.000	1.273	1.033	0.000	0.000	0.000	30.0
1.457	1.359	0.000	0.000	1.157	0.987	0.000	0.000	0.000	33.0
1.311	1.350	0.000	0.000	1.175	1.018	0.000	0.000	0.000	35.0
1.021	1.492	0.000	0.000	1.004	0.849	0.000	0.000	0.000	40.0
0.957	1.406	0.000	0.000	1.149	1.039	0.000	0.000	0.000	45.0

Table III-8. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 146.3° .

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.404	0.863	0.482	0.403	0.639	0.533	0.455	0.172	0.457		0.23725
2	0.386	0.863	0.474	0.398	0.587	0.481	0.441	0.161	0.447		0.21262
3	0.481	1.083	0.551	0.491	0.799	0.601	0.539	0.207	0.497		0.26823
4	0.441	1.029	0.549	0.472	0.765	0.600	0.535	0.188	0.512		0.25883
5	0.324	0.700	0.391	0.338	0.545	0.450	0.381	0.132	0.388		0.18136
6	0.254	0.602	0.334	0.277	0.447	0.372	0.309	0.115	0.329		0.14168
7	0.334	0.676	0.382	0.320	0.504	0.431	0.344	0.124	0.359		0.17338
8	0.292	0.598	0.347	0.288	0.458	0.377	0.329	0.120	0.345		0.17897
9	0.316	0.622	0.389	0.308	0.484	0.398	0.367	0.137	0.356		0.19627
10	0.345	0.708	0.386	0.339	0.532	0.444	0.386	0.152	0.374		0.20526
11	0.363	0.742	0.433	0.363	0.569	0.470	0.404	0.148	0.421		0.20222
12	0.282	0.598	0.345	0.284	0.457	0.368	0.321	0.118	0.361		0.16103
13	0.331	0.682	0.413	0.353	0.552	0.443	0.399	0.148	0.410		0.20430
14	0.228	0.472	0.245	0.209	0.347	0.279	0.231	0.091	0.263		0.14175

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.745	1.628	0.836	0.000	1.050	0.523	0.555	0.000	0.389	5.0	0.23662
2	0.506	1.397	0.683	0.000	0.759	0.385	0.362	0.000	0.293	7.5	0.20801
3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.00000
4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.00000
5	0.172	0.546	0.261	0.000	0.240	0.182	0.128	0.000	0.182	15.0	0.17981
6	0.133	0.292	0.152	0.000	0.119	0.131	0.059	0.000	0.166	17.5	0.13856
7	0.158	0.383	0.194	0.000	0.146	0.167	0.079	0.000	0.174	20.0	0.17208
8	0.102	0.219	0.128	0.000	0.114	0.165	0.055	0.000	0.075	22.3	0.17762
9	0.092	0.195	0.134	0.000	0.091	0.179	0.051	0.000	0.050	25.0	0.19228
10	0.053	0.152	0.073	0.000	0.071	0.100	0.011	0.000	0.081	30.0	0.20394
11	0.037	0.097	0.061	0.000	0.044	0.038	0.022	0.000	0.002	35.0	0.20029

Table III-9. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 146.3°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.266	-0.277	-0.240	0.000	-0.217	0.007	-0.088	0.000	0.070	5.0
-0.127	-0.218	-0.168	0.000	-0.121	0.088	0.076	0.000	0.173	7.5
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
0.272	0.105	0.172	0.000	0.352	0.388	0.471	0.000	0.324	15.0
0.273	0.305	0.333	0.000	0.565	0.442	0.707	0.000	0.288	17.5
0.320	0.243	0.291	0.000	0.534	0.409	0.636	0.000	0.311	20.0
0.454	0.432	0.428	0.000	0.602	0.356	0.771	0.000	0.658	22.3
0.527	0.496	0.454	0.000	0.716	0.339	0.851	0.000	0.844	25.0
0.815	0.664	0.723	0.000	0.871	0.645	1.546	0.000	0.661	30.0
0.982	0.879	0.847	0.000	1.109	1.083	1.265	0.000	0.000	35.0

Table III-10. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 144.9° .

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.587	0.743	0.709	0.591	0.972	0.780	0.685	0.263	0.569		0.28624
2	0.589	1.390	0.759	0.627	1.133	0.846	0.695	0.272	0.609		0.26530
3	0.488	1.079	0.595	0.512	0.889	0.672	0.577	0.228	0.508		0.22230
4	0.451	0.920	0.549	0.468	0.737	0.610	0.513	0.194	0.438		0.19846
5	0.480	1.119	0.581	0.498	0.822	0.634	0.897	0.190	0.476		0.20225
6	0.450	0.946	0.529	0.453	0.745	0.599	0.510	0.185	0.457		0.17415
7	0.319	0.667	0.380	0.322	0.556	0.429	0.359	0.141	0.325		0.13593
8	0.402	0.869	0.487	0.416	0.690	0.539	0.470	0.177	0.416		0.17400
9	0.372	0.754	0.429	0.371	0.620	0.489	0.416	0.158	0.387		0.15888
10	0.483	1.016	0.579	0.497	0.844	0.647	0.555	0.201	0.475		0.20600

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	1.229	0.512	0.523	0.000	0.530	0.955	0.992	0.000	0.559	0.0	0.28475
2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.00000
3	0.773	1.741	0.671	0.000	0.822	0.485	0.371	0.000	0.206	12.5	0.22062
4	0.467	1.267	0.802	0.000	0.689	0.496	0.356	0.000	0.181	15.0	0.19669
5	0.353	0.945	0.475	0.000	0.535	0.297	0.249	0.000	0.169	17.5	0.19695
6	0.228	0.555	0.328	0.000	0.343	0.255	0.164	0.000	0.064	20.0	0.17147
7	0.116	0.235	0.154	0.000	0.148	0.191	0.064	0.000	0.010	22.5	0.13693
8	0.134	0.295	0.191	0.000	0.178	0.218	0.078	0.000	0.018	25.5	0.17146
9	0.070	0.163	0.096	0.000	0.097	0.125	0.000	0.000	0.001	30.0	0.15888
10	0.081	0.179	0.110	0.000	0.110	0.155	0.000	0.000	0.000	35.0	0.20388

Table III-11. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 144.9°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.323	0.000	0.000	0.000	0.000	-0.090	-0.163	0.000	0.005	5.0
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
-0.203	-0.211	-0.056	0.000	0.031	0.138	0.189	0.000	0.389	12.5
-0.019	-0.143	-0.168	0.000	0.025	0.086	0.155	0.000	0.381	15.0
0.121	0.062	0.076	0.000	0.175	0.318	0.545	0.000	0.439	17.5
0.288	0.225	0.200	0.000	0.330	0.365	0.487	0.000	0.846	20.0
0.444	0.456	0.395	0.000	0.578	0.354	0.752	0.000	1.497	22.5
0.470	0.463	0.400	0.000	0.581	0.386	0.776	0.000	1.368	25.5
0.727	0.664	0.649	0.000	0.806	0.591	0.000	0.000	2.813	30.0
0.769	0.749	0.717	0.000	0.879	0.615	0.000	0.000	0.000	35.0

Table III-12. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 138.9°.

Initial Absorbances for Indicated Bands (K)

Pel- let No:	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.656	1.035	0.737	0.501	0.855	0.650	0.551	0.199	0.476		0.18587
2	0.425	0.682	0.403	0.342	0.558	0.459	0.387	0.144	0.364		0.15008
3	0.432	0.687	0.411	0.362	0.578	0.470	0.409	0.163	0.355		0.15800
4	0.431	0.688	0.532	0.456	0.716	0.594	0.509	0.196	0.461		0.19754
5	0.430	0.673	0.507	0.457	0.702	0.560	0.484	0.174	0.436		0.18792
6	0.557	1.259	0.668	0.584	0.937	0.747	0.642	0.244	0.547		0.25445
7	0.484	1.054	0.584	0.512	0.851	0.649	0.573	0.209	0.486		0.21954
8	0.444	0.906	0.547	0.477	0.733	0.610	0.541	0.201	0.460		0.20157
9	0.470	0.954	0.552	0.480	0.746	0.616	0.533	0.200	0.468		0.20927
10	0.445	0.965	0.562	0.492	0.754	0.639	0.569	0.223	0.439		0.20408

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.869	0.000	1.147	0.694	1.444	0.658	0.671	0.162	0.387	5.0	0.18407
2	0.276	0.522	0.301	0.198	0.341	0.219	0.172	0.035	0.087	10.0	0.14807
3	0.529	1.268	0.557	0.362	0.590	0.434	0.302	0.073	0.157	15.0	0.15800
4	0.509	1.273	0.625	0.382	0.704	0.432	0.385	0.098	0.183	20.0	0.19754
5	0.331	0.776	0.448	0.280	0.483	0.278	0.236	0.056	0.111	25.0	0.18612
6	0.451	1.119	0.611	0.374	0.654	0.370	0.322	0.089	0.155	30.0	0.25445
7	0.274	0.625	0.377	0.232	0.403	0.291	0.198	0.049	0.081	35.0	0.21468
8	0.186	0.434	0.282	0.184	0.284	0.180	0.147	0.040	0.044	40.0	0.20043
9	0.150	0.298	0.226	0.000	0.196	0.000	0.109	0.000	0.000	45.0	0.20668
10	0.117	0.244	0.170	0.000	0.000	0.000	0.080	0.000	0.000	50.0	0.20408

Table III-13. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 138.9°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.126	0.000	-0.196	-0.145	-0.232	-0.009	-0.090	0.084	0.086	5.0
0.181	0.110	0.121	0.231	0.208	0.315	0.346	0.609	0.616	10.0
-0.088	-0.266	-0.132	-0.000	-0.010	0.034	0.131	0.349	0.356	15.0
-0.072	-0.267	-0.070	0.076	0.007	0.138	0.121	0.300	0.402	20.0
0.109	-0.066	0.049	0.209	0.158	0.300	0.308	0.488	0.591	25.0
0.092	0.051	0.039	0.194	0.156	0.305	0.299	0.439	0.549	30.0
0.238	0.218	0.181	0.333	0.315	0.339	0.452	0.617	0.766	35.0
0.376	0.317	0.285	0.412	0.410	0.527	0.564	0.700	1.019	40.0
0.490	0.500	0.382	0.000	0.575	0.000	0.683	0.000	0.000	45.0
0.581	0.597	0.518	0.000	0.000	0.000	0.850	0.000	0.000	50.0

Table III-14. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 131.9°.

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.267	0.524	0.334	0.300	0.416	0.378	0.351	0.159	0.281		0.20707
2	0.361	0.745	0.485	0.438	0.614	0.547	0.517	0.232	0.410		0.28630
3	0.324	0.639	0.432	0.386	0.544	0.497	0.445	0.198	0.338		0.24394
4	0.240	0.497	0.316	0.284	0.391	0.354	0.327	0.147	0.257		0.18109
5	0.341	0.631	0.404	0.364	0.514	0.463	0.421	0.181	0.329		0.24059
6	0.354	0.647	0.432	0.400	0.546	0.493	0.474	0.219	0.365		0.25108
7	0.313	0.606	0.392	0.355	0.506	0.463	0.413	0.185	0.329		0.23976
8	0.328	0.618	0.399	0.368	0.525	0.466	0.433	0.197	0.349		0.24000
9	0.297	0.585	0.395	0.361	0.498	0.465	0.426	0.198	0.321		0.21475
10	0.229	0.519	0.307	0.282	0.390	0.356	0.328	0.157	0.272		0.17235

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.712	1.443	0.518	0.550	1.069	0.605	0.649	0.191	0.421	5.0	0.20606
2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.00000
3	0.810	1.765	1.032	0.661	1.235	0.686	0.711	0.204	0.399	15.0	0.23921
4	0.588	1.453	0.739	0.483	0.888	0.516	0.514	0.153	0.267	20.0	0.18109
5	0.589	1.206	0.692	0.476	0.828	0.528	0.517	0.166	0.284	25.0	0.23943
6	0.654	1.806	0.797	0.516	0.968	0.632	0.581	0.184	0.338	30.0	0.24211
7	0.503	1.406	0.741	0.486	0.781	0.458	0.463	0.148	0.253	40.0	0.23832
8	0.430	1.048	0.643	0.424	0.689	0.395	0.387	0.129	0.215	50.0	0.23559
9	0.245	0.592	0.366	0.243	0.368	0.322	0.212	0.065	0.089	60.0	0.21270
10	0.162	0.355	0.238	0.171	0.221	0.274	0.137	0.046	0.038	70.0	0.17000

Table III-15. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 131.9°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.428	-0.442	-0.192	-0.266	-0.412	-0.206	-0.269	-0.081	-0.177	5.0
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0
-0.407	-0.450	-0.387	-0.242	-0.364	-0.149	-0.212	-0.023	-0.081	15.0
-0.389	-0.466	-0.369	-0.230	-0.356	-0.164	-0.197	-0.017	-0.016	20.0
-0.239	-0.283	-0.235	-0.118	-0.209	-0.059	-0.092	0.037	0.061	25.0
-0.282	-0.462	-0.282	-0.126	-0.264	-0.123	-0.104	0.061	0.017	30.0
-0.209	-0.368	-0.279	-0.138	-0.191	0.003	-0.051	0.095	0.112	40.0
-0.126	-0.237	-0.215	-0.069	-0.126	0.064	0.041	0.177	0.203	50.0
0.080	-0.009	0.029	0.167	0.128	0.155	0.299	0.480	0.553	60.0
0.143	0.159	0.104	0.212	0.242	0.108	0.373	0.530	0.848	70.0

Table III-16. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1°.

Initial Absorbances for Indicated Bands (K)

Pel- let										Pellet	
No:	3000	1700	1440	1310	1300	1175	900	760	650	Time	Weight(g)
1	0.321	0.625	0.411	0.351	0.487	0.433	0.362	0.207	0.269		0.24242
2	0.263	0.559	0.317	0.262	0.356	0.309	0.309	0.127	0.262		0.20672
3	0.258	0.514	0.318	0.277	0.376	0.314	0.310	0.139	0.280		0.19426
4	0.265	0.515	0.325	0.295	0.411	0.374	0.354	0.157	0.286		0.20180
5	0.286	0.626	0.357	0.302	0.414	0.335	0.331	0.153	0.268		0.21637
6	0.387	0.784	0.559	0.455	0.640	0.578	0.532	0.251	0.427		0.29098
7	0.264	0.559	0.321	0.262	0.367	0.303	0.317	0.135	0.270		0.21581
8	0.232	0.455	0.297	0.271	0.378	0.338	0.314	0.138	0.259		0.18866
9	0.289	0.562	0.328	0.263	0.388	0.300	0.296	0.123	0.246		0.18623
10	0.248	0.510	0.326	0.302	0.412	0.373	0.345	0.168	0.278		0.19542
11	0.272	0.602	0.335	0.275	0.388	0.320	0.331	0.153	0.283		0.20837
12	0.360	0.716	0.473	0.428	0.586	0.531	0.514	0.232	0.392		0.27480
13	0.356	0.703	0.459	0.418	0.591	0.528	0.491	0.219	0.392		0.27060
14	0.209	0.409	0.272	0.252	0.353	0.315	0.299	0.144	0.243		0.15500
15	0.287	0.426	0.284	0.254	0.341	0.317	0.305	0.141	0.239		0.16548
16	0.217	0.426	0.273	0.248	0.341	0.314	0.292	0.136	0.236		0.16500
17	0.327	0.641	0.434	0.397	0.548	0.499	0.458	0.209	0.359		0.25806

Absorbances After Indicated Heating Intervals

[illegible]

Table III-18. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1°.

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.276	0.574	0.382	0.346	0.470	0.434	0.402	0.183	0.324		0.24242
2	0.277	0.544	0.360	0.324	0.449	0.404	0.373	0.175	0.300		0.20277
3	0.252	0.494	0.320	0.290	0.406	0.363	0.335	0.157	0.278		0.20672
4	0.250	0.497	0.334	0.311	0.413	0.379	0.355	0.170	0.280		0.19426
5	0.212	0.423	0.289	0.271	0.357	0.333	0.314	0.152	0.253		0.21637
6	0.236	0.499	0.325	0.283	0.407	0.376	0.350	0.163	0.264		0.21581
7	0.249	0.526	0.350	0.315	0.443	0.392	0.372	0.188	0.303		0.18623
8	0.273	0.546	0.360	0.327	0.451	0.412	0.384	0.178	0.303		0.20837
9	0.245	0.325	0.341	0.316	0.424	0.390	0.367	0.172	0.292		0.19977
10	0.248	0.492	0.329	0.299	0.405	0.375	0.353	0.158	0.279		0.19936

Absorbances After Indicated Heating Intervals

[illegible]

Table III-19. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 158.1°.

[illegible]

Table III-20. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in KBr at 161.0° .

Initial Absorbances for Indicated Bands (K)

Pellet No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.246	0.485	0.315	0.296	0.388	0.358	0.345	0.264	0.247		0.19271
2	0.239	0.468	0.311	0.281	0.381	0.348	0.331	0.152	0.254		0.18469
3	0.342	0.661	0.447	0.418	0.553	0.524	0.481	0.214	0.386		0.27537
4	0.223	0.454	0.289	0.270	0.355	0.340	0.320	0.153	0.275		0.18426
5	0.275	0.543	0.362	0.326	0.454	0.415	0.392	0.181	0.317		0.22685
6	0.306	0.618	0.395	0.362	0.488	0.463	0.422	0.189	0.335		0.23371
7	0.193	0.344	0.237	0.218	0.283	0.270	0.249	0.123	0.192		0.21651
8	0.264	0.538	0.365	0.343	0.450	0.426	0.408	0.202	0.319		0.22134
9	0.301	0.571	0.392	0.363	0.488	0.447	0.433	0.203	0.338		0.23575
10	0.365	0.712	0.455	0.398	0.565	0.516	0.474	0.208	0.370		0.26525

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.561	1.264	0.681	0.509	0.868	0.544	0.534	0.153	0.296	1.0	0.19271
2	0.561	1.457	0.678	0.447	0.840	0.524	0.463	0.133	0.258	2.0	0.18392
3	0.737	1.737	0.888	0.574	1.100	0.654	0.615	0.185	0.356	3.0	0.27165
4	0.350	0.916	0.478	0.284	0.558	0.355	0.321	0.097	0.152	4.0	0.18132
5	0.324	0.773	0.420	0.273	0.474	0.269	0.236	0.092	0.122	5.0	0.22447
6	0.251	0.621	0.315	0.220	0.369	0.218	0.175	0.046	0.092	6.0	0.23707
7	0.122	0.239	0.146	0.103	0.153	0.123	0.073	0.018	0.023	7.0	0.21489
8	0.151	0.331	0.179	0.124	0.200	0.166	0.086	0.000	0.032	8.0	0.21905
9	0.122	0.263	0.156	0.000	0.163	0.000	0.075	0.000	0.000	9.0	0.23271
10	0.105	0.219	0.122	0.000	0.127	0.000	0.050	0.000	0.000	10.0	0.26525

Table III-21. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 161.0°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.358	-0.416	-0.334	-0.236	-0.349	-0.182	-0.190	0.239	-0.079	1.0
-0.373	-0.495	-0.340	-0.203	-0.346	-0.180	-0.148	0.057	-0.009	2.0
-0.339	-0.426	-0.304	-0.143	-0.305	-0.102	-0.113	0.057	0.028	3.0
-0.203	-0.312	-0.226	-0.030	-0.203	-0.025	-0.009	0.191	0.250	4.0
-0.076	-0.158	-0.069	0.073	-0.023	0.183	0.215	0.287	0.412	5.0
0.092	0.004	0.104	0.222	0.127	0.333	0.389	0.619	0.566	6.0
0.196	0.156	0.206	0.321	0.264	0.337	0.533	0.828	0.922	7.0
0.239	0.207	0.304	0.436	0.347	0.404	0.673	0.000	0.988	8.0
0.386	0.332	0.395	0.000	0.471	0.000	0.753	0.000	0.000	9.0
0.540	0.513	0.571	0.000	0.647	0.000	0.979	0.000	0.000	10.0

Pellet	No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.280	0.573	0.380	0.353	0.468	0.435	0.404	0.183	0.312			0.22054
2	0.353	0.684	0.453	0.420	0.577	0.530	0.497	0.226	0.388			0.26421
3	0.330	0.624	0.425	0.398	0.531	0.494	0.472	0.221	0.371			0.26325
4	0.359	0.677	0.455	0.413	0.568	0.517	0.499	0.228	0.386			0.28017
5	0.266	0.528	0.349	0.334	0.446	0.421	0.393	0.197	0.324			0.22065
6	0.247	0.497	0.323	0.304	0.411	0.382	0.353	0.165	0.285			0.21451
7	0.247	0.470	0.314	0.289	0.395	0.368	0.350	0.165	0.282			0.20848
8	0.327	0.633	0.449	0.404	0.549	0.511	0.496	0.229	0.359			0.26354
9	0.259	0.505	0.332	0.305	0.411	0.386	0.362	0.168	0.278			0.20438
10	0.258	0.524	0.332	0.309	0.434	0.384	0.360	0.172	0.281			0.19270

[illegible]

Table III-23. PLOTFA (See Appendix I) for Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in KBr at 167.0°

[illegible]

Table III-24. Absorbances Used to Determine k' for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5° .

Initial Absorbances for Indicated Bands (K)

Pel- let No.	3000	1700	1440	1310	1300	1175	900	760	650	Time	Pellet Weight(g)
1	0.192	0.354	0.247	0.213	0.302	0.282	0.261	0.133	0.242		0.16618
2	0.195	0.396	0.270	0.224	0.330	0.299	0.267	0.136	0.235		0.17171
3	0.251	0.512	0.335	0.292	0.445	0.402	0.360	0.186	0.319		0.23055
4	0.241	0.481	0.348	0.287	0.432	0.394	0.370	0.200	0.330		0.21538
5	0.193	0.394	0.257	0.222	0.335	0.305	0.266	0.132	0.244		0.17407
6	0.239	0.419	0.271	0.214	0.329	0.297	0.270	0.128	0.347		0.20991
7	0.264	0.525	0.338	0.289	0.448	0.395	0.349	0.183	0.314		0.21984
8	0.242	0.566	0.356	0.317	0.469	0.428	0.387	0.204	0.347		0.25051
9	0.250	0.520	0.355	0.305	0.449	0.397	0.365	0.192	0.327		0.25090
10	0.246	0.332	0.201	0.167	0.255	0.233	0.206	0.113	0.295		0.23402

Absorbances After Indicated Heating Intervals

	3000	1700	1440	1210	1220	1175	900	760	650	Time	Pellet Weight(g)
1	0.699	1.348	0.611	0.512	0.733	0.596	0.291	0.161	0.409	3.0	0.15989
2	0.504	0.795	0.402	0.270	0.496	0.411	0.246	0.112	0.341	5.0	0.16813
3	0.639	1.172	0.619	0.380	0.724	0.561	0.387	0.157	0.442	6.0	0.23920
4	0.399	0.619	0.300	0.000	0.304	0.396	0.165	0.000	0.244	7.0	0.20910
5	0.207	0.321	0.196	0.000	0.179	0.289	0.138	0.000	0.194	8.0	0.16919
6	0.207	0.338	0.214	0.000	0.199	0.350	0.165	0.000	0.210	9.0	0.20215
7	0.171	0.322	0.191	0.000	0.176	0.286	0.108	0.000	0.170	10.0	0.21443
8	0.126	0.311	0.151	0.000	0.156	0.161	0.026	0.000	0.000	11.0	0.23558
9	0.000	0.165	0.063	0.000	0.084	0.094	0.000	0.000	0.000	13.0	0.24540
10	0.000	0.202	0.000	0.000	0.121	0.118	0.000	0.000	0.000	15.0	0.22593

Table III-25. PLOTFA (See Appendix I) for the Indicated Bands (K) for the Thermal Decarboxylation of Malonic Acid in RbBr at 158.5°.

3000	1700	1440	1310	1220	1175	900	760	650	Time
-0.578	-0.598	-0.410	-0.398	-0.402	-0.341	-0.063	-0.100	-0.245	3.0
-0.422	-0.312	-0.182	-0.090	-0.186	-0.148	0.028	0.073	-0.171	5.0
-0.390	-0.344	-0.250	-0.098	-0.195	-0.129	-0.015	0.090	-0.126	6.0
-0.233	-0.123	0.051	0.000	0.139	-0.014	0.339	0.000	0.119	7.0
-0.042	0.077	0.105	0.000	0.262	0.011	0.274	0.000	0.087	8.0
0.046	0.076	0.086	0.000	0.202	-0.088	0.198	0.000	0.203	9.0
0.178	0.202	0.237	0.000	0.396	0.129	0.499	0.000	0.257	10.0
0.258	0.233	0.345	0.000	0.451	0.397	1.151	0.000	0.000	11.0
0.000	0.488	0.740	0.000	0.720	0.614	0.000	0.000	0.000	13.0
0.000	0.200	0.000	0.000	0.309	0.280	0.000	0.000	0.000	15.0

where A_t is the absorbance of the reactant remaining at time t . Substituting equation (7) into equation (4) and assuming constant density gives,

$$k't = \log \frac{A_o W_t}{A_t W_o}$$

where $k' = k/2.303$.

The first order rate constants for a given reaction temperature can now be obtained by plotting $\log \left[A_o W_t / A_t W_o \right]$ (PLOTFA of Appendix I) vs. t . The result should be a straight line of slope k' from which k can be obtained.

Figures III-5 through III-13 show the rate constant plots for the KBr malonic acid system at 158.0° and for the RbBr-malonic acid system at 158.5° . The 900 K absorption band in the RbBr-malonic acid system gave such random points that no sensible line could be drawn through them. Tables III-8 through III-25 give the data from the other experimental runs both in the raw data and as the factor, $\log \left[A_o W_t / A_t W_o \right]$ (PLOTFA).

Determination of Thermodynamic Quantities

From the experimental rate constants and their corresponding temperatures several thermodynamic parameters can be determined for the thermal decarboxylation of malonic acid.

These thermodynamic quantities are determined on the basis of the theory of absolute reaction rates. According to the theory of absolute reaction rates

$$k = \frac{k_b t}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

where

k_b = Boltzmann's Constant

h = Planck's Constant

R = Universal gas constant (cal/mole. deg)

ΔS^\ddagger = entropy of activation

ΔH^\ddagger = enthalpy of activation

T = absolute temperature

This equation shows that a plot of $\log k/T$ versus $1/T$ should yield a straight line of slope $-\Delta H^\ddagger / 2.303R$ and with an intercept at $(1/T = 0)$ of $\log \left[\frac{k_b}{h} + \frac{\Delta S^\ddagger}{2.303R} \right]$. A plot of $\log k/T$ versus $1/T$ for the five absorption bands of malonic acid used in this work is shown in Figure III-14. The plot gives a value for ΔH^\ddagger of 25.7 ± 1 kcal/mol and a value of ΔS^\ddagger of $-10.5 \pm$ cal/mole. deg. The data which gave rise to this plot are given in Table III-26 along with the values for k obtained in RbBr.

The free energy change for the reaction (ΔG_T^\ddagger) can be calculated at a given temperature from the equation

$$\Delta G_T^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

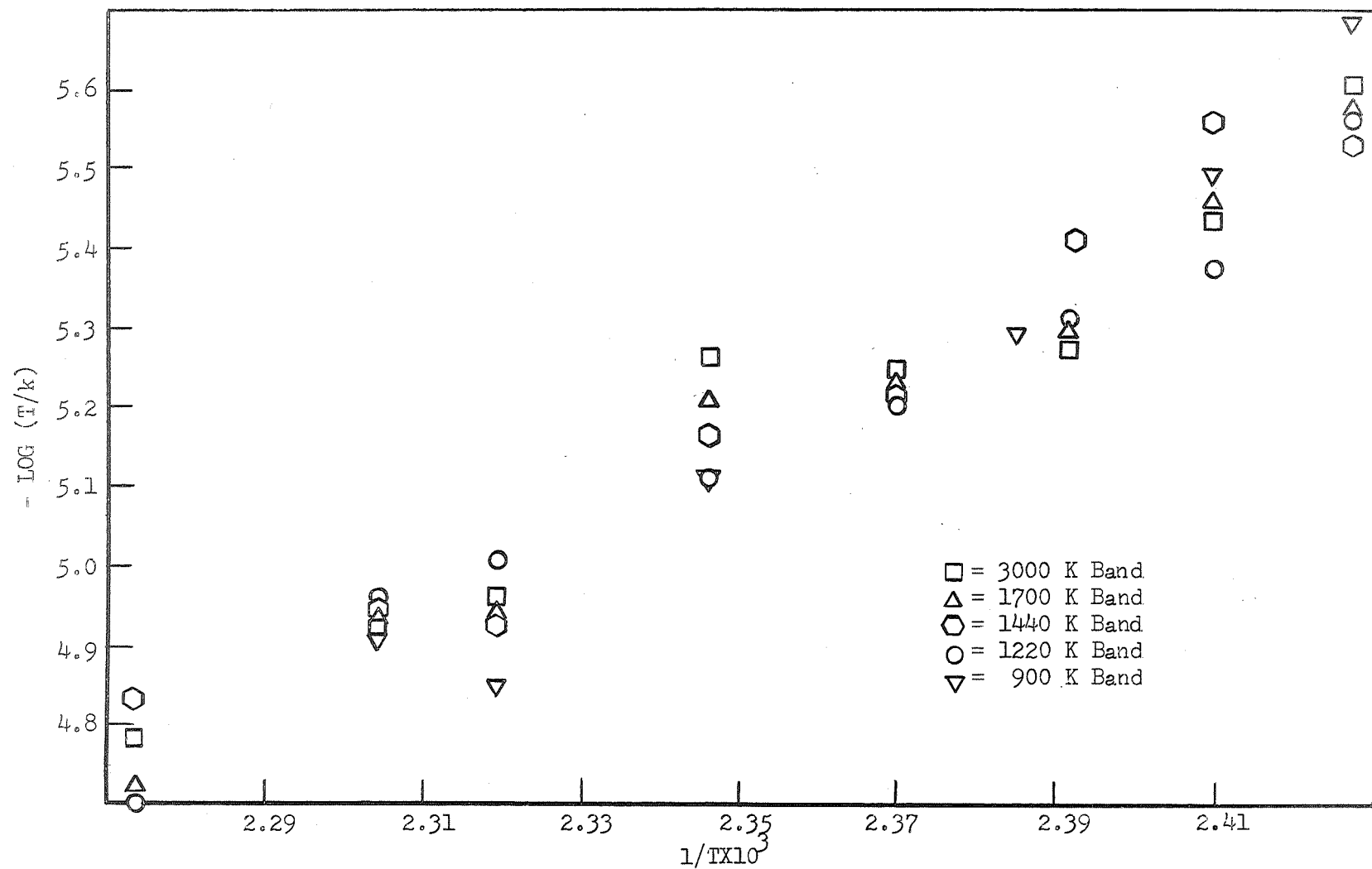


Figure III-14. Combined Enthalpy of Activation Plot for the Thermal Decarboxylation of Malonic Acid in KBr at Temperatures from 138.9° to 167.0°.

Using a temperature of 135° , a value for $\Delta G_{135}^{\ddagger}$ of 30.0 ± 1 kcal/mole is obtained.

Critique of the Multipellet Method

In the earlier stages of this research two different methods were developed for obtaining kinetic data for the thermal decarboxylation of malonic acid in alkali halide media. One of these methods, the single pellet method, involved heating a single pellet, in which the reactant was incorporated, for a known period of time. The pellet was then repressed and its infrared spectrum obtained. This procedure was then repeated as many times as necessary to drive the desired reaction to completion. The method, although used by other researchers³³⁻³⁷, has rather serious drawbacks. One drawback is its vulnerability to accidents. If a pellet is broken or otherwise becomes unusable in the course of an experiment, then it is necessary to repeat the entire experiment using another pellet. Another more serious drawback is related to pellet heatup time. The pellet heatup time introduces a lag into the measured time during a kinetic run. This necessitates some correction of the elapsed time before use in obtaining rate constants. When a pellet is heated for several time intervals the errors in correction for the heating times accumulate causing an expansion or contraction of the time scale and a corresponding error in determination of the rate constants. This error is particularly detrimental in kinetic runs at temperatures which produce short half lines (5-16 minutes) since the accumulated error tends to become a sizable quantity in the total heating time.

Mainly as a means of circumventing the problem of heatup time, another procedure was developed for obtaining the necessary kinetic data. This method involves the use of several different pellets, all from the same mixture of malonic acid and salt. It is called, in this work, "the multipellet method."

The procedure used to obtain data by the multipellet method has been described in the experimental section of Part III and the treatment of the data obtained is described in a previous section. The multipellet method yielded consistent results. The multipellet method does, however, generate quite a large amount of data, making the use of an electronic computer a real asset.

In the initial stages of a kinetic run the absorbance of the pellets showed an increase. As can be seen in Figures III-5 through III-13, in the initial stages of the decarboxylation of malonic acid, the quantity $\text{Log} \left[\frac{W_t A_o}{W_o A_t} \right]$ or PLOTFA (See Appendix I) is negative in sign. This can occur from two causes, (1) a loss in pellet weight and/or (2) an initial increase in absorbance. The loss in pellet weight is a natural consequence of the repressing procedure and is corrected for in the data handling sequence. Moreover, if pellet weight alone were responsible for the negative sign, a loss in pellet weight of 50% would be required to make PLOTFA negative by approximately 0.3. The normal weight loss upon repressing is approximately 0.001g or 0.5%.

An initial increase in absorbance appears to be a more reasonable explanation of the negative sign for PLOTFA. An explanation

might be as follows: the working temperature is above the melting point of malonic acid (136°) so that the material might fuse and begin to disperse throughout the pellet. A more uniform dispersion should result in an increase in absorbance of malonic acid, in the pellets.

Hartman³⁵ solved the problem of changes in the initial absorbances of his compounds by subjecting his pellets to an annealing period. However, his working temperature was $200-300^{\circ}$ which allowed annealing at 100° without preliminary decomposition. In the present work, the annealing procedure is impractical since temperatures as low as 80° were found to bring about thermal decomposition of malonic acid and lower temperatures had no effect upon the initial absorbances of the pellets. Fortunately, the inability to anneal the pellets did not create major problems since the time required for the absorbances to reach maximum values was approximately 2 minutes at 140° , after which a decrease in absorbance occurs due to decomposition of the sample. It is interesting to note that the time required for the absorptions to reach maxima is approximately equal to the pellet heatup time. This would indicate that the anomalous absorption behavior is indeed dependent upon either the fusion and dispersion of malonic acid in the pellets, or the phase change of malonic acid. It is believed from the present research, that the changes in initial absorbances are the result of better dispersion of the sample in the pellets.

In the use of the quantity $\log \left[\frac{A_{o} W_t}{A_t W_o} \right]$, another advantage of the multipellet method is apparent. Since the pellet weight and the

absorbance appear as ratios in the logarithm factor some of the errors due to dispersion of the sample in the matrix are reduced. For instance if the original mixture were not quite homogeneous, the error associated with the inhomogeneity would produce a small relative error since the corrections for inhomogeneity would appear as additive terms in both the divisor and the dividend. If this were the case, a slight tailing of the resultant plots would be expected and is indeed found, in some cases.

Reaction Mechanisms for the Thermal Decarboxylation of Organic Acids

Frankel, et al³¹ have proposed a mechanism for thermal decarboxylation of acids which has been generally accepted. Frankel's mechanism involves the formation of an activated complex between an electrophilic carbonyl carbon atom and a nucleophilic center on the solvent. This mechanism is supported by the fact that k decreases with increasing solvent basicity. Frankel, et al³¹ also noted a linear dependence of the rate of decarboxylation upon the concentration of a strong amine base, pyridine. They also discovered that the reaction rate dependence disappeared at a 1:1 mole ratio of amine base to malonic acid, indicating that the reaction is bimolecular. On the basis of the above information, Frankel proposed two possible mechanisms for the thermal decarboxylation of malonic acid, showing no preference between the two mechanisms. These mechanisms are depicted in Figure III-15 with pyridine as the complexing species.

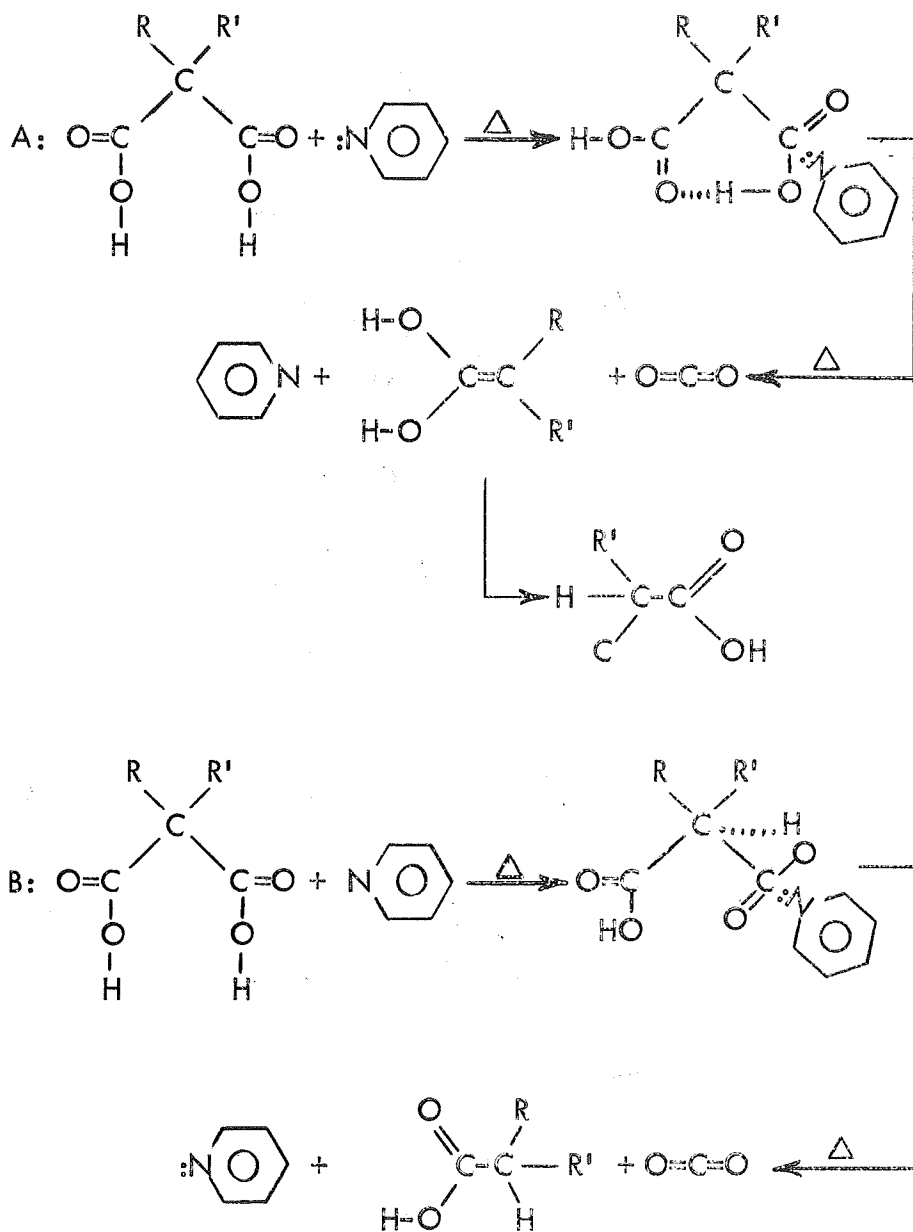


Figure III-15. Reaction Mechanism Proposed³ for the Thermal Decarboxylation of Malonic Acid.

Kenyon and Ross³⁰ observed that unsymmetrically disubstituted malonic acid does not produce optically active acetic acid upon decarboxylation. This would support mechanism A, Figure III-15, since production of a racemic mixture of d- and l-unsymmetrically disubstituted acetic acid would require formation of a carbon-carbon double bond at some point in the reaction mechanism.

Blades and Wallbridge¹⁴ observed that malonic acid exhibits no kinetic isotope effect upon deuteration. This absence of an isotope effect suggests that the rate determining step in the decarboxylation is the breaking of a carbon-carbon bond rather than the formation or dissociation of a hydrogen bond.

Clark^{23,25}, as a result of his studies of the thermal decarboxylation of malonic acid in numerous solvents, has proposed that malonic acid decomposes by the same mechanism as do α -unsaturated acids in general (basically mechanism A in Figure III-15). This proposition is supported by Clark²³ in reference to isokinetic temperature plots. When ΔH^\ddagger is plotted versus ΔS^\ddagger for a given series of reactions in various solvents, the result is a straight line of slope T, the isokinetic temperature. Petersen and co-authors³⁸ have pointed out the limitations in the use of this formulation in drawing valid conclusions. Petersen et al established requirements which must be satisfied by the data used before the conclusion drawn from use of the data can have valid meanings. The data obtained by Clark²⁶ appear to satisfy these requirements. Clark has observed that, for all of the

solvents studied thus far as media for the decarboxylation of malonic acid, the ΔH^\ddagger and ΔS^\ddagger values when plotted form a straight line with a slope of 422° K (149° C). The ΔH^\ddagger and ΔS^\ddagger values for the decarboxylation of molten malonic acid also fall on the same straight line as those from various solvents.

Table III-27 shows the ΔH^\ddagger , ΔS^\ddagger and $\Delta G_{135^\circ\text{C}}^\ddagger$ values obtained by Clark for the decarboxylation of malonic acid in various selected solvents, as well as the values for molten malonic acid²², and the values obtained in this work for malonic acid in KBr. It can be seen that the values obtained in KBr are comparable to those obtained in other solvents, indicating that the same mechanism prevails in each case. It can also be seen that the ΔH^\ddagger value for decarboxylation of malonic acid in KBr is significantly lower than that obtained for molten malonic acid. This could be the result of an activation effect due to the alkali halide medium.

Comparison of the reaction rates in KBr with those obtained in RbBr reveals no significant differences in reaction rates throughout the series. This is the expected effect if the above mechanism were the true reaction mechanism, since the nucleophilic halide anion would be responsible for the activation effect. Investigations of the effect of the anion upon the reaction rate would be most meaningful but are impractical in this case due to the interfering double decomposition reaction.

An interesting observation is the fact found in the research that solid malonic acid also undergoes thermal decarboxylation. This

Table III-27. Activation Parameters for the Thermal Decarboxylation of Malonic Acid in Several Media.

	ΔH^\ddagger Kcal/mole	ΔS^\ddagger eu/mole	ΔG_{135}^\ddagger (kcal/mole)
1-Butanol ²²	27.2	-4.4	29.0
1-Hexanol ²²	26.0	-7.6	29.1
2-Ethylhexanol-1 ²²	24.8	-10.4	29.05
Diisobutylcarbitol ²²	24.8	-10.7	29.16
Cyclohexanol ²²	23.0	-15.0	29.13
Acetanilide ²²	19.85	-22.66	29.1
Molten Malonic Acid ²⁵	35.8	+11.9	31.0
Malonic Acid in KBr	25.7	-10.5	30.0

reaction, although slow, proceeds at a measurable rate at 80° ; a temperature well below the melting point of malonic acid (136°). An 80° kinetic run was made in an attempt to establish whether the solid state decomposition occurred from the β - or α -phase of malonic acid. The malonic acid decomposed slowly at 80° which is 25° below the reported phase transition temperature. Therefore, it appears that malonic acid can also decompose from the β phase. No lower temperature runs were attempted since the reaction half-life of approximately 6 weeks at 80° was well beyond the attention span of the researcher involved.

Conclusion

In conclusion, it should be pointed out that the multipellet method, as outlined in this work, enables the collection of data on the decarboxylation of malonic acid at temperatures higher than were previously possible. The nature of the method allows the study of reactions with half-lives as low as 4 minutes without significant problems. This allowed the use of reaction temperatures which were 15° higher than those previously reported. Further refinement of the method should allow the study of reactions with even lower half lives.

This work has further shown the feasibility of determining reaction rate parameters in solid salt media. The results obtained, in this case, agree well with those obtained in other media and also

with those obtained in the molten state. However, as pointed out in Part II, of this dissertation, there are obstacles to overcome prior to use of the pressed pellet method.

PART III

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APPENDIX

The program listed below was written by the author, especially to handle the data obtained from the "multipellet" method (See General Introduction and Experimental and Part III of this dissertation). It was modified by Charles S. Shoemaker to produce output on the Calcamp Plotter. The program was written in Fortran IV and is for use on an IBM 7040 Computer.

The program as written is for use with first order reactions but can be modified for reactions of other order. For example, this could be accomplished by changing statement number 1240 to read,

$$\text{PLOTFA(N,K)} = ((\text{STDABS(N,K)}/\text{BASEWT(N)}) - (\text{TIMEAB(N,K)}/\text{TIMEWT(M)})) /$$

$$((\text{STDABS(N,K)} * \text{TIMEAB(N,K)} * .20000) / (\text{BASEWT(N)} * \text{TIMEWT(N)}))$$

If this is done the punched card output should be discarded.

The Calcamp plotter output is a plot of PLOTFA versus time for the absorption bands followed during the course of the experiment. A different character is used on the plot for each of the bands followed during the course of the experiment.

A legend appears on the plot identifying which character represents which absorption band. These character identifications are built into the program but may be changed by referring to ISN 366 through 414.

The program also produces a punched card output in the format accepted by the LSKIN¹* program.

*C. E. Detar and D. F. Detar, "Least Squares Treatment of First Order Rate Data," Program 80, Quantum Chemistry Program Exchange, Indiana University (1967).

The order of the cards in the data deck is shown below along with reproduction of the data cards described.

Card Group 1: This card is a control card which establishes the limits of several do-loops in the program. It should have 5 numbers on it. A reproduction of the card is shown below as Card number 1. The necessary numbers are:

- (1) I RUN - This is a data identification number chosen by the researcher. It should contain a maximum of five digits punched in an I5 format in card columns 1-5, right justified.
- (2) NUMHEL- This is the number of pellets heated in the kinetic run. The maximum allowable number is established in the DIMENSION statements. NUMHEL should occupy card columns 6-10 in an I5 format.
- (3) NUMDIL- This is the number of pellets originally prepared and used to establish base absorbances. If a series of spectra were not used to establish a base absorbance, particular care should be taken in choosing which of the statements numbered 1240 is to be used. NUMDIL should be a number, whose maxima is established in the DIMENSION statement, punched in card columns 11-15 in an I5 format.
- (4) NUMBAL - This is the number of absorption bands which are to be used in the calculations. The maximum of NUMBAL is established in the DIMENSION statement.

NUMBAL should occupy card columns 16-20 in an I5 Format.

- (5) TEM1 - This is the temperature of the kinetic run whose data are being analyzed. TEM1 should be punched in card columns 21-26 in an F6.1 format.

Card Group 2: These cards begin the raw data to be processed. They have the baseline absorbance, or transmittances, from the initial spectra in the format shown below as Card Number 2. They should also contain the initial pellet weights in card columns 46-52 in an F7.5 format. The total number of cards in this group should equal NUMDIL.

Card Group 3: These cards should contain the peak absorbances or transmittance readings of the absorption bands of the initial pellets. The total number of cards in this group should equal NUMDIL. The format of these cards is given below as the reproduction labelled Card Number 3.

Card Group 4: These cards should contain the baseline absorbances or transmittances from the spectra of the heated pellets. They should also contain the heating times punched in card columns 46-51 in an F6.1 format, and, in addition, the weights of the heated pellets in card columns 52-58 in an F7.5 format. The total number of cards in this group should equal NUMHEL. The format of this group of data cards is illustrated below as Card Number 4.

Card Group 5: These cards should contain the absorbance or transmittance readings of the absorption bands in the spectra of the heated

pellets. The total number of cards in this group should equal NUMHEL. The format of this card group is shown below as Card Number 3.

If data from more than one kinetic run are to be analyzed NUMDAT (see the fourth comment in the program listing) should be changed and the successive data sets queued, repeating all the data card formats of card groups 1 through 5.


```

C *****
C   THIS PROGRAM TAKES THE MEASURED ABSORBANCE OR TRANSMITTANCE
C   * VALUES AND CALCULATES 1) THE VARIANCES FOR EACH BAND MEASURED
C   * AND 2) THE FACTORS TO BE PLOTTED AGAINST THE HEATING TIME. THE
C   * PROGRAM ALSO PRODUCES A PLOTTER OUTPUT TAPE WHICH IS THEN FED INTO
C   * THE CALCOMP PLOTTER TO OBTAIN THE PLOT OF TIME VS. PLOTTING FAC-
C   * TOR. THE PROGRAM ALSO PRODUCES A PUNCHED CARD OUTPUT IN THE FOR-
C   * MAT REQUIRED BY THE LSKINI PROGRAM. THE ABSORBANCES WHICH ARE
C   * PUNCHED OUT ARE CORRECTED TO A STANDARD DISK WEIGHT OF .20 GRAMS.
C *****
C
C *****
C   *
C   * THE FIRST VALUE OF STDBAS WHICH IS READ INTO STORAGE IS A TEST
C   * VALUE WHICH DETERMINES WHETHER THE PROGRAM HANDLES THE INPUT VAL-
C   * UES AS ABSORBANCES OR AS TRANSMITTANCES. THE VALUE OF STDBAS(1,1)
C   * SHOULD NEVER BE SET EQUAL TO ZERO.
C   *
C *****
C
C *****
C   *
C   * IT IS NECESSARY TO HAVE THE INDEXING NUMBERS OF THE ORIGINAL
C   * DISKS MATCHED WITH THOSE OF THE HEATED DISKS. THIS SHOULD BE
C   * DONE BY PUTTING THE APPROPRIATE NUMBER OF ZERO CARDS INTO THE
C   * DATA DECK AT THE POSITION CORRESPONDING TO THE UNMATCHED CARD.
C   *
C *****
C
1  DIMENSION BUF(2000)
2  DIMENSION Y1(20),Y2(20),Y3(20),Y4(20),Y5(20),Y6(20),Y7(20),Y8(20),
  1Y9(20),X(20),Y(400)
3  DIMENSION STDBAS(50,25),PEAKHT(50,25),BASTIM(50,25),TIMEHT(50,25),
  1TIME(50),TIMEWT(50),SUMABS(50),STDABS(50,25),ABSSTD(50),AVEABS(50),
  2STDDEV(50),TIMEAB(50,25),PLOTFA(50,25),VARIAN(50),BASEWT(50),TEM1
  3(10),NUMDI1(10),NUMHE1(10),NUMAN1(10),NUMBA1(10),IRUN(10)
4  100 FORMAT(9F5.3,F7.5)
5  101 FORMAT(9F6.3,6X,F8.5)
6  103 FORMAT(15,15,15,15,F6.1)
7  110 FORMAT(9F5.3)
10 111 FORMAT(9F7.3)
11 120 FORMAT(9F5.3,F6.1,F7.5)
12 121 FORMAT(9F7.3,F6.1,F8.5)
13 141 FORMAT(5X,I3,10X,F8.5)
14 142 FORMAT(1H1/////33X,23HTHESE ARE THE VARIANCES/)
15 143 FORMAT(7X,1HN,7X,8HVARIANCE//)
16 144 FORMAT(33X,24HFOR KINETIC RUN NUMBER ,I5,3H-A-//)
17 150 FORMAT(9E10.5,F6.1)
20 151 FORMAT(5X,I3,3X,9(F7.3,4X),F6.1)
21 152 FORMAT(1H1/////14X,55HTHESE ARE THE PLOTTING FACTORS FOR KINETIC RUN
  1 NUMBER ,I5,3H-A-//)
22 153 FORMAT(7X,1HN,6X,4H3000,5X,4H1700,5X,4H1440,5X,4H1310,5X,4H1220,5X

```

1,4H1175,6X,3H900,6X,3H760,6X,3H650,5X,4HTIME//)

23 154 FORMAT(27X,19H THE TEMPERATURE IS ,F6.1//)

24 5 FORMAT(1H1)

25 160 FORMAT(10X,F8.5)

130

```
C
C *****
C *
C * NUMDAT IS A PART OF THE PROGRAM WHICH ALLOWS THE HANDLING OF SUC *
C * CESSIVE SETS OF DATA WHICH WERE OBTAINED IN DIFFERENT RUNS. IT IS *
C * SIMPLY THE NUMBER OF SETS OF DATA WHICH ARE TO BE ANALYZED. *
C *
C *****
C
26 NUMDAT= 1
27 DO 3001 MMM=1,NUMDAT
30 WRITE(6,5)
C
C *****
C *
C * NUMHET IS THE NUMBER OF DISKS HEATED IN THE KINETIC RUN. *
C *
C *****
C
C *****
C * NUMBAN IS THE NUMBER OF BANDS WHOSE ABSORBANCES WERE FOLLOWED *
C *
C *****
C
C *****
C *
C * NUMDIS IS THE ORIGINAL NUMBER OF DISKS *
C *
C *****
C
31 7 READ(5,103) IRUN(M),NUMHE1(M),NUMDI1(M),NUMBA1(M),TEM1(M)
32 NUMBAN=NUMBA1(M)
33 NUMANL=NUMAN1(M)
34 NUMDIS=NUMDI1(M)
35 NUMHET=NUMHE1(M)
36 TEMP=TEM1(M)
37 9 DO 10 N=1,NUMDIS
40 10 READ(5,100) STDBAS(N,1),STDBAS(N,2),STDBAS(N,3),STDBAS(N,4),STDBAS
1(N,5),STDBAS(N,6),STDBAS(N,7),STDBAS(N,8),STDBAS(N,9),BASEWT(N)
42 19 DO 20 N=1,NUMDIS
43 20 READ(5,110) PEAKHT(N,1),PEAKHT(N,2),PEAKHT(N,3),PEAKHT(N,4),PEAKHT
1(N,5),PEAKHT(N,6),PEAKHT(N,7),PEAKHT(N,8),PEAKHT(N,9)
45 29 DO 30 N=1,NUMHET
46 30 READ(5,120) BASTIM(N,1),BASTIM(N,2),BASTIM(N,3),BASTIM(N,4),BASTIM
1(N,5),BASTIM(N,6),BASTIM(N,7),BASTIM(N,8),BASTIM(N,9),TIME(N),TIME
2WT(N)
50 39 DO 40 N=1,NUMHET
51 40 READ(5,110) TIMEHT(N,1),TIMEHT(N,2),TIMEHT(N,3),TIMEHT(N,4),TIMEHT
1(N,5),TIMEHT(N,6),TIMEHT(N,7),TIMEHT(N,8),TIMEHT(N,9)
```

```

53 41 CONTINUE
54 50 IF(STDBAS(1,1).GT.PEAKHT(1,1)) GO TO 60
57 51 IF(STDBAS(1,1).LT.PEAKHT(1,1)) GO TO 80
62 60 DO 65 K=1,NUMBAN
63 DO 65 N=1,NUMDIS
64 IF(STDBAS(N,K)-PEAKHT(N,K)) 62,62,64
65 62 STDABS(N,K)=0.0
66 GO TO 69
67 64 STDBAS(N,K)=ALOG10(1.00/STDBAS(N,K))
70 PEAKHT(N,K)=ALOG10(1.00/PEAKHT(N,K))
71 65 STDABS(N,K)=PEAKHT(N,K)-STDBAS(N,K)
74 69 CONTINUE
75 70 DO 75 K=1,NUMBAN
76 DO 75 N=1,NUMHET
77 IF(BASTIM(N,K)-TIMEHT(N,K)) 71,71,72
100 71 TIMEAB(N,K)=0.0
101 GO TO 75
102 72 BASTIM(N,K)=ALOG10(1.00/BASTIM(N,K))
103 TIMEHT(N,K)=ALOG10(1.00/TIMEHT(N,K))
104 74 TIMEAB(N,K)=TIMEHT(N,K)-BASTIM(N,K)
105 75 CONTINUE
110 GO TO 200
111 80 DO 85 K=1,NUMBAN
112 DO 85 N=1,NUMDIS
113 IF(PEAKHT(N,K)-STDBAS(N,K)) 82,82,84
114 82 STDABS(N,K)=0.0
115 GO TO 85
116 84 STDABS(N,K)=PEAKHT(N,K)-STDBAS(N,K)
117 85 CONTINUE
122 DO 96 K=1,NUMBAN
123 DO 96 N=1,NUMHET
124 IF(TIMEHT(N,K)-BASTIM(N,K)) 92,92,94
125 92 TIMEAB(N,K)=0.0
126 GO TO 96
127 94 TIMEAB(N,K)=TIMEHT(N,K)-BASTIM(N,K)
130 96 CONTINUE

```

C

C

C-----WE NOW BEGIN THE PROCESS OF CALCULATING THE VARIANCES OF THE MEASURED
 C-----BANDS IN THE ORIGINAL UNHEATED DISKS.USING THE FORMULA VARIANCE =
 C----- $(\text{SUMMATION}(\{X-X(\text{AVERAGE})\}^2))/(N-1)$

C

C

```

133 155 FORMAT(1H1/////10X,33HTHESE ARE THE AVERAGE ABSORBANCES/10X,28HFOR
      1 DISKS OF .20000G WEIGHTS//)
134 200 WRITE(6,155)
135 201 DO 1200 K=1,NUMBAN
136 SUMABS(K)=0.00
137 250 DO 1000 N=1,NUMDIS
140 IF(STDABS(N,K).EQ.0.0) GO TO 1000
143 260 ABSSTD(N)=STDABS(N,K)*0.20/BASEWT(N)

```

C

C

C-----WE HAVE NOW CALCULATD THE ABSORBANCE WHICH THIS DISK WOULD HAVE
 C-----HAD IF THE DISK HAD WEIGHED 0.20000 GRAMS.

```

C
C
144      SUMABS(K)=SUMABS(K)+ABSSTD(N)
145 1000 CONTINUE
147      HNUMDI=NUMDIS
150 1010 AVEABS(K)=SUMABS(K)/HNUMDI
151      WRITE(6,160) AVEABS(K)
152 1020 STDDEV(K)=0.00
153 1030 DO 1100 N=1,NUMDIS
154 1040 STDDEV(K)=STDDEV(K)+((ABS(ABSSTD(N)))-(ABS(AVEABS(K))))**2
155 1100 CONTINUE
157 1110 VARIAN(K)=STDDEV(K)/(HNUMDI-1.00)
160 1200 CONTINUE
C
C
C-----WE NOW CALCULATE THE PLOTTING FACTORS FOR THE FIRST ORDER REACTION
C
C
162 1210 DO 1400 K=1,NUMBAN
163 7000 FORMAT(I2)
164      WRITE(7,7000) K
165 1211 DO 1300 N=1,NUMHET
166 1221 IF (TIMEAB(N,K)-0.0) 1222,1222,1240
167 1222 PLOTFA(N,K)=0.0
170 1223 GO TO 1250
C
C *****
C *
C * IF THE ABSORBANCES OF THE ORIGINAL DISKS(STDABS(N,K)) ARE
C * AVAILABLE, USE THE CARD WITH A ONE IN COLUMN 78. IF THEY ARE
C * NOT AVAILABLE, USE THE CARD WITH A TWO IN COLUMN 78.
C *
C *****
171 1240 PLOTFA(N,K)=ALOG10(STDABS(N,K)*TIMEWT(N)/(TIMEAB(N,K)*BASEWT(N)))
C1240 PLOTFA=ALOG10((AVEABS(K)*TIMEWT(N,K))/(TIMEAB(N,K)*(0.20000)))
C
C *****
C *
C * THIS SECTION CALCULATES THE CORRECTED ABSORBANCES AND PRODUCES
C * A PUNCHED CARD OUTPUT IN THE FORM REQUIRED BY THE LSKINI PROGRAM.
C *
C *****
172 1250 XYZ=TIMEAB(N,K)*(0.20/TIMEWT(N))
173 7001 FORMAT(E10.5,10X,E10.5)
174      WRITE(7,7001) TIME(N),XYZ
175 1300 CONTINUE
177 1400 CONTINUE
201 156 FORMAT(1H1/////10X,22HTHESE ARE THE RAW DATA//)
202      WRITE(6,156)
203 1499 DO 1501 N=1,NUMDIS
204 1500 WRITE(6,101) STDBAS(N,1),STDBAS(N,2),STDBAS(N,3),STDBAS(N,4),STDBA
1S(N,5),STDBAS(N,6),STDBAS(N,7),STDBAS(N,8),STDBAS(N,9),BASEWT(N)
205 1501 CONTINUE

```

```

207 1599 DO 1601 N=1,NUMDIS
210 1600 WRITE(6,111) PEAKHT(N,1),PEAKHT(N,2),PEAKHT(N,3),PEAKHT(N,4),PEAKH
133
1T(N,5),PEAKHT(N,6),PEAKHT(N,7),PEAKHT(N,8),PEAKHT(N,9)
211 1601 CONTINUE
213 1699 DO 1701 N=1,NUMHET
214 1700 WRITE(6,121) BASTIM(N,1),BASTIM(N,2),BASTIM(N,3),BASTIM(N,4),BASTI
1M(N,5),BASTIM(N,6),BASTIM(N,7),BASTIM(N,8),BASTIM(N,9),TIME(N),TIM
2EWT(N)
215 1701 CONTINUE
217 1799 DO 1801 N=1,NUMHET
220 1800 WRITE(6,111) TIMEHT(N,1),TIMEHT(N,2),TIMEHT(N,3),TIMEHT(N,4),TIMEH
1T(N,5),TIMEHT(N,6),TIMEHT(N,7),TIMEHT(N,8),TIMEHT(N,9)
221 1801 CONTINUE
223 180 FORMAT(1H1/////15X,25HTHESE ARE THE ABSORBANCES//)
224 WRITE(6,180)
225 3050 DO 3060 N=1,NUMDIS
226 WRITE(6,101) STDABS(N,1),STDABS(N,2),STDABS(N,3),STDABS(N,4),STDAB
1S(N,5),STDABS(N,6),STDABS(N,7),STDABS(N,8),STDABS(N,9),BASEWT(N)
227 3060 CONTINUE
231 190 FORMAT(////)
232 WRITE(6,190)
233 3070 DO 3080 N=1,NUMHET
234 WRITE(6,121) TIMEAB(N,1),TIMEAB(N,2),TIMEAB(N,3),TIMEAB(N,4),TIMEA
1B(N,5),TIMEAB(N,6),TIMEAB(N,7),TIMEAB(N,8),TIMEAB(N,9),TIME(N),TIM
2EWT(N)
235 3080 CONTINUE
237 1897 WRITE(6,142)
240 WRITE(6,144) IRUN(M)
241 1898 WRITE(6,143)
242 1899 DO 1901 N=1,NUMBAN
243 1900 WRITE(6,141) N,VARIAN(N)
244 1901 CONTINUE
246 1997 WRITE(6,152) IRUN(M)
247 1999 WRITE(6,154) TEMP
250 1998 WRITE(6,153)
251 DO 2000 N=1,NUMHET
252 2000 WRITE(6,151) N,PLOTFA(N,1),PLOTFA(N,2),PLOTFA(N,3),PLOTFA(N,4),PLO
1TFA(N,5),PLOTFA(N,6),PLOTFA(N,7),PLOTFA(N,8),PLOTFA(N,9),TIME(N)
C *****
C *WE NOW CHECK FOR AND REMOVE ANY ROW WHERE TIME(I) = 0.0 AND
C * PLOTFA(I,1) = 0.0 *
C *****
254 I=1
255 N= NUMHET
256 2002 CONTINUE
257 IF(TIME(I)-0.)2040,2005,2040
260 2005 IF(PLOTFA(I,1)-0.)2040,2015,2040
261 2015 N=N-1
262 IF(I-N)2025,2025,2050
263 2025 DO 2035 M=I,N
264 TIME(M)= TIME(M+1)
265 DO 2035 K=1,9
266 PLOTFA(M,K)= PLOTFA(M+1,K)
267 2035 CONTINUE
272 GO TO 2002

```

```

273 2040 I=I+1
274      IF(I-N) 2002,2002,2050
275 2050 CONTINUE
276      WRITE(6,152) IRUN(1)
277      WRITE(6,154) TEMP
300      WRITE(6,153)
301      DO 2020 I=1,N
302      WRITE(6,151) I,PLOTFA(I,1),PLOTFA(I,2),PLOTFA(I,3),PLOTFA(I,4),PLOTFA(I,5),PLOTFA(I,6),PLOTFA(I,7),PLOTFA(I,8),PLOTFA(I,9),TIME(I)
303 2020 CONTINUE
C      *****
C      * WE NOW CONVERT THE COLUMNS OF PLOTFA INTO THE LINEAR ARRAYS *
C      * Y1, Y2, - - - , Y9. EACH ARRAY REPRESENTS THE PLOT FACTORS *
C      * OF ONE BAND *
C      *****
305      DO 2055 I=1,N
306      X(I)= TIME(I)
307      Y1(I)= PLOTFA(I,1)
308      Y2(I)= PLOTFA(I,2)
309      Y3(I)= PLOTFA(I,3)
310      Y4(I)= PLOTFA(I,4)
311      Y5(I)= PLOTFA(I,5)
312      Y6(I)= PLOTFA(I,6)
313      Y7(I)= PLOTFA(I,7)
314      Y8(I)= PLOTFA(I,8)
315      Y9(I)= PLOTFA(I,9)
316
C      *****
C      * WE NOW FORM Y(I) A LINEAR ARRAY FROM PLOTFA A RECTANGULAR *
C      * ARRAY Y(I) IS USED FOR SCALING THE Y AXIS *
C      *****
C
C      IF PROGRAM IS TO SCALE ITSELF , THEN USE CARDS WITH 1 IN COLUMN
C      74. IF PROGRAMER IS TO SCALE THE GRAPH HIMSELF, THEN USE CARDS
C      WITH 2 IN COLUMN 74.
C
320      L=I*9
321      DO 2055 M=1,9
322      LL= L+1-M
323      Y(LL)= PLOTFA(I,M)
324 2055 CONTINUE
327      CALL PLOTS(BUF,2000)
330      CALL SCALE(X,30.,N,1,10.0)
331      NN=N*9
332      CALL SCALE(Y,20.,NN,1,10.0)
C
C      N1= N+1
C      N2= N+2
C      X(N2)=
C      X(N1)=
C      Y(1)=
C      Y(2)=
C
C      *****

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C      * WE NOW INSERT THE MINMUM VALUE AND SCALE IN UNITS PER INCH IN *
C      * EACH ARRAY TO BE PLOTTED AT POSITIONS YI(N+1) AND YI(N+2). *
C      ****
333    DO 2060 I=1,2
C      IN=I
334    II= N+I
335    IN=NN+I
336    Y1(II)= Y(IN)
337    Y2(II)= Y(IN)
340    Y3(II)= Y(IN)
341    Y4(II)= Y(IN)
342    Y5(II)= Y(IN)
343    Y6(II)= Y(IN)
344    Y7(II)= Y(IN)
345    Y8(II)= Y(IN)
346    Y9(II)= Y(IN)
347  2060 CONTINUE
351    MM=N+1
352    MN=N+2
353    CALL AXIS(0.,05.,4HTIME,-4,30.,0.,X(MM),X(MN),10.)
354    CALL AXIS(0.,0.,6HY AXIS,6,20.,90.,Y1(MM),Y1(MN),10.)
C
C
C      * IF AN ARRAY IS NOT TO BE PLOTTED, THEN A C SHOULD BE PUNCHED *
C      * IN COLUMN ONE IN FRONT OF CALL LINE(X,YI, ), WHERE YI IS *
C      * THE ARRAY TO BE NEGLECTED. *
C
C
355    CALL LINE(X,Y1,N,1,-1,14)
356    CALL LINE(X,Y2,N,1,-1,12)
357    CALL LINE(X,Y3,N,1,-1,11)
360    CALL LINE(X,Y4,N,1,-1,10)
361    CALL LINE(X,Y5,N,1,-1, 5)
362    CALL LINE(X,Y6,N,1,-1, 2)
363    CALL LINE(X,Y7,N,1,-1,6)
364    CALL LINE(X,Y8,N,1,-1,0)
365    CALL LINE(X,Y9,N,1,-1, 7)
366    CALL SYMBOL(9.,21.,0.42,26HFIRST ORDER KINETICS GRAPH,0.,26)
367    CALL SYMBOL(2.,14.0.,.175,15H*****,.0.,15)
370    CALL SYMBOL(2.,13.8.,.175,15H*          *.0.,15)
371    CALL SYMBOL(2.,13.6.,.175,15H* =3000 CM-1 *.0.,15)
372    CALL SYMBOL(2.3,13.7.,.175,14.0.,-1)
373    CALL SYMBOL(2.,13.4.,.175,15H* =1700 CM-1 *.0.,15)
374    CALL SYMBOL(2.3,13.5.,.175,12.0.,-1)
375    CALL SYMBOL(2.,13.2.,.175,15H* =1440 CM-1 *.0.,15)
376    CALL SYMBOL(2.3,13.3.,.175,11.0.,-1)
377    CALL SYMBOL(2.,13.0.,.175,15H* =1310 CM-1 *.0.,15)
400    CALL SYMBOL(2.3,13.1.,.175,10.0.,-1)
401    CALL SYMBOL(2.,12.8.,.175,15H* =1225 CM-1 *.0.,15)
402    CALL SYMBOL(2.3,12.9.,.175, 5.0.,-1)
403    CALL SYMBOL(2.,12.6.,.175,15H* =1175 CM-1 *.0.,15)
404    CALL SYMBOL(2.3,12.7.,.175, 2.0.,-1)
405    CALL SYMBOL(2.,12.4.,.175,15H* = 900 CM-1 *.0.,15)
406    CALL SYMBOL(2.3,12.5.,.175, 6.0.,-1)
407    CALL SYMBOL(2.,12.2.,.175,15H* = 760 CM-1 *.0.,15)

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270

185

410 CALL SYMBOL(2.3,12.3,.175,0,0.,-1)
411 CALL SYMBOL(2.,12.0,.175,15H* = 650 CM-1 *,0.,15)
412 CALL SYMBOL(2.3,12.1,.175,7,0.,-1)
413 CALL SYMBOL(2.,11.8,.175,15H* *,0.,15)
414 CALL SYMBOL(2.,11.6,.175,15H***** ,0.,15)
415 CALL PLOT(35.,0.,-3)
416 3001 CONTINUE
420 CALL PLOTS(0.,0.,999)
421 3000 STOP
422 END

ABSTRACT

The behavior of malonic acid in various alkali halide matrices upon application of heat has been investigated. It was found that there are three distinct types of behavior exhibited by malonic acid when it is mixed with an alkali halide salt, pressed into a pellet and the pellet heated. These three reactions are characterized as follows: (1) "normal" behavior, i.e., decarboxylation of the malonic acid to form acetic acid and carbon dioxide; (2) salt formation, a double decomposition reaction between the malonic acid and the alkali halide used, resulting in formation of malonate salts; (3) "anomalous" behavior, tentatively attributed to formation of a solid solution between malonic acid and the alkali halide matrix used (observed only in the CsCl and "anhydrous" NaBr matrices).

The first of the above mentioned reactions has been studied extensively in the matrix, KBr, and partially in RbBr. First order rate constants for the thermal decarboxylation of malonic acid in KBr and RbBr have been obtained and, in the case of KBr, these rate constants have been used to obtain activation parameters for the thermal decarboxylation reaction. The activation parameters obtained are $\Delta H^\ddagger = 25.7 \pm 1$ kcal/mole. $\Delta S^\ddagger = 10.5 \pm 1$ cal/deg. mole and $\Delta G_{1350}^\ddagger = 30.0 \pm 1$ kcal/mole. No difference in the rate of decarboxylation was noted between KBr and RbBr.

A section of the dissertation is devoted to the assignment of infrared absorption bands to fundamental modes of vibrations for the malonic acid molecule in salt matrices. This assignment has been facilitated by using a simplified symmetry treatment in which crystalline malonic acid is considered to consist of two independent symmetry units.


VITA


Lowell Allen Cosby was born September 29, 1942 in Seth, West Virginia. He received his elementary education in the schools of Boone, Calhoun and Logan counties and attended high school at Logan High School in Logan, West Virginia. He then enrolled at Alderson-Broadbush College in September 1960 under a Hospital Work Scholarship and received his Bachelor of Science degree from said institution in May 1964 with a major in Chemistry.

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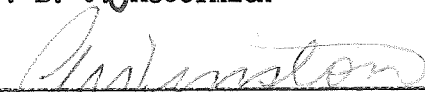
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APPROVAL OF THE EXAMINING COMMITTEE


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